THE PHYTOAVAILABILITY OF CADMIUM IN SOME NEW ZEALAND SOILS

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This thesis is dedicated in loving memory

of my father

William Gray

Abstract of a thesis submitted in partial fulfilment of the requirements for the Degree Doctor of Philosophy

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by Colin William Gray

In New Zealand, phosphate fertiliser use has resulted in an accumulation of cadmium (Cd) in some pasture soils, and has led to an elevation in Cd concentrations in pasture species growing on these soils. While there is an abundance of literature on the soil chemistry of Cd, there is shortage of data dealing with soil Cd concentrations that are relevant to New Zealand soils, typically < 1.5 μg Cd g^{-1} soil. The purpose of this study was to determine some of the factors that affect the phytoavailability of Cd in soils at the low Cd concentrations relevant to New Zealand conditions, and to ultimately identify management strategies to minimise Cd uptake into plants.

In a study using six soils to investigate the effect of soil pH on sorption/desorption of both native and added Cd, it was revealed that with increasing pH (between pH 4.9 - pH 6.2) there was a substantial reduction in the concentration of both native and added Cd desorbed from soils using 0.01 M $Ca(NO_3)_2$. Conversely it was found that there was an increase in the concentration of added Cd sorbed as pH increased from 4.9 to 6.2. Soil organic carbon was also identified as playing an important role in controlling sorption and desorption of Cd. Regression analysis using a larger set of soils (29), indicated that soil pH, organic carbon and total soil Cd were the most dominant soil variables controlling Cd solubility. In addition, the same three soil parameters were important for governing desorption of native Cd into soil solution. Soil pH and organic carbon were important in the sorption Cd, while CEC along with soil pH were important in controlling added Cd desorption. In addition, increasing soil pH was shown in a glasshouse study to significantly decrease plant Cd concentrations, in five different plant species.

There was evidence of immobilisation of Cd in soils as a result of increased contact time between the soil and added Cd. Results from an incubation study, where Cd was added to

the soil as $Cd(NO_3)_2$, revealed that for four very different soils, there was a decrease in the concentration of Cd desorbed into solution using 0.01 M $Ca(NO_3)_2$ with an increasing contact period of up to 70 days. Additional evidence of Cd immobilisation with contact time was derived from a long-term superphosphate trial, where Cd had been added to soil, fertiliser application ceased and the same soil re-sampled 21 years later. Results from the trial indicated that during this 21 year hiatus, the proportion of Cd in soluble forms, as determined by a chemical fractionation, decreased, while there was an increase in Cd in residual fractions. A study of the same soil which had received annual superphosphate fertiliser application for 44 years, revealed through chemical fractionation, that there was an increase in Cd associated with the exchangeable and organic fractions with time, however there was still a substantial proportion of Cd in non-available residual forms. Similarly, for 12 topsoil samples in a separate study, while there was a wide range in the concentrations of Cd associated with individual soil fractions, the greatest concentration of Cd was associated with the organic and residual fractions, with substantial proportions of Cd added as a result of fertiliser application present in the residual, and presumably non-phytoavailable, fraction.

In a glasshouse study, the concentrations of Cd in a number of vegetable, pasture, and cereal species was investigated. Plant Cd concentrations varied greatly between different plant species and soil types. All plants were within the maximum residue limit (MRL) for the Cd content of all foodstuffs intended for human consumption. In an evaluation of soil extractants that are commonly used to predict plant Cd concentrations, it was found that a unbuffered or neutral extractant such as $CaCl_2$, NH_4OAc, or $Ca(NO_3)_2$ which was sensitive to soil pH was a suitable predictor of plant Cd concentrations.

An investigation into the rate of Cd accumulation in soil from a long-term (44 yr) superphosphate fertiliser trial was carried out. Results indicated that there had been a significant accumulation of Cd in soil that has been subject to long term superphosphate fertiliser application relative to the control plot. On the high fertiliser treatment (376 kg superphosphate ha^{-1} yr^{-1}), Cd was estimated to have accumulated at a rate of 7.8 g ha^{-1} yr^{-1}. There was also evidence of movement of Cd down the soil profile in this irrigated soil.

This study has identified several management options available for the control of Cd phytoavailability in soils. The maintenance of a soil pH within a target range of 5.8-6.0 will not only increase sorption of Cd but will decrease desorption of Cd and reduce Cd solubility. The adoption of farming practices which maintain adequate organic matter levels in the soil should be encouraged. The selection of P fertilisers with low Cd concentrations is to be promoted to reduce soil Cd concentrations. Finally, as a management strategy, a 'hands off' approach may be suitable given that there seems to be fixation of Cd in soil with increased residence time.

Key words: Sorption, desorption, solubility, native Cd, added Cd, isotherms, pH, organic carbon, contact time, pot trial, plants, Cd fractionation, phosphate fertiliser.

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Chapter 1

Introduction

1.1 Introduction

In New Zealand, phosphate fertiliser use has resulted in an accumulation of cadmium (Cd) in some pasture soils. In a recent national survey examining the Cd status of 86 native and 312 pasture soil sites, Roberts *et al.* (1994) found that concentrations of soil Cd at pasture sites were double those on their native counterparts. Cadmium concentrations at pastoral sites were highly correlated with total soil phosphorus, linking this increase in total soil Cd concentration to phosphate fertiliser inputs.

Elevated Cd concentrations on pasture soils have been shown to lead to enhanced Cd uptake in pastoral species. Sheep and other ruminants grazing this pasture can absorb a small, yet significant proportion of this Cd, some of which is subsequently stored in the liver and kidneys of the animal. Because Cd turnover in the kidneys and liver is very slow, the Cd content increases with the age of the animal (Lee *et al.* 1996a). As a result, Cd concentrations in the offal in these animals could pose a threat to New Zealand's offal export trade, with Cd concentrations used as non-tariff barriers against trade of these products.

In the current environmental climate, there has been an increasing public awareness and concern for food quality, particularly in relation to contamination by pesticide residues and heavy metal contaminants such as Cd. The maximum permitted concentration (MPC) of Cd in foodstuffs in New Zealand is currently set at 1 mg kg^{-1} FW (exception some shellfish), however this limit is currently under re-examination with concentrations likely to be harmonised with Australia under a review by the Australian and New Zealand Food Authority by 1999 (Table 1.1).

This study was undertaken because of the lack of information with regard to soil cadmium chemistry and plant uptake of Cd at concentrations in the soil that are relevant to New Zealand agricultural systems. A large proportion of the existing literature involves Cd concentrations often orders of magnitude greater than those encountered in New Zealand

agricultural systems, where Cd has for the most part accumulated slowly in soils, through the use of phosphatic fertilisers and to concentrations often less than 1.5 μg Cd g^{-1}.

Secondly, studies have often involved Cd added to soils as soluble inorganic salts or as sewage sludge, which have been shown to behave differently to Cd added to soil in fertilisers, which also makes it difficult to extrapolate the results of such work to New Zealand agriculture.

Table 1.1 Proposed cadmium concentrations in foodstuffs for human consumption under review by the Australian and New Zealand Food Authority

Food product	**μg Cd g^{-1} FW**
Kidney of cattle, sheep and pig	2.5
Liver of cattle, sheep and pig	1.5
molluscs excluding dredge/bluff oysters)	1.25
leafy vegetables	0.1
root and tuber vegetables	0.1
wheat	0.1
meat flesh of cattle, sheep and pig	0.05

1.2 Project rationale and objective

The purpose of the present study was to examine the phytoavailability of Cd in soils using low Cd concentrations that are applicable to New Zealand agriculture, and to ultimately develop management strategies to minimise Cd uptake into plants.

Chapter 2

Literature Review

2.1 Chemistry of Cd

Cadmium (Cd) was discovered in 1817 by Strohmeyer of Germany, who isolated it from calamine (zinc carbonate). The name cadmium is derived from *cadmia*, the ancient Greek name for calamine (Nriagu 1980).

Cadmium is a soft, ductile, silver-white, electropositive metal with an atomic weight of 112.4 and specific gravity of 8.642 g cm^{-3}. At atomic number 48, Cd is positioned between zinc (Zn) and mercury (Hg) in Group IIb of the Periodic Table of elements. Its electron configuration is $1s^2 2s^2 3p^6 3d^{10} 4s^2 4d^{10} 5s^2$. With melting and boiling points of 321°C and 767°C respectively, and a heat of vaporisation of 26.8 kcal mol^{-1}, Cd is considered to be a relatively volatile metal (Cotton and Wilkinson 1966).

2.2 Cadmium in soil parent materials

Cadmium is found naturally in soils, water, plants and other environmental matrices not affected by pollution. The mean Cd content in the earth's crust is estimated to be around 0.11mg kg^{-1} (Bowen 1979), with Cd concentrations in crustal rocks varying from 1 to 90 mg kg^{-1} (Kabata-Pendias 1992). The range and mean Cd concentrations for some common igneous, metamorphic and sedimentary rocks are presented in Table 2.1. Cadmium concentrations are relatively low in igneous and metamorphic rocks. Cadmium tends to accumulate by sedimentation as indicated by the high concentrations in sedimentary rocks, with some shales in particular unusually high in Cd. For example, Lund *et al.* (1981) found Cd concentrations as high as 90 mg kg^{-1} in shales along the Pacific Coast in the United States.

Geochemically, Cd is closely associated with Zn, with both elements having similar ionic structures and electronegativities, and to a lesser extent with minerals of lead (Pb) and copper (Cu). Most Cd produced is recovered as a by-product during the smelting of zinc ore (sphalerite), in which Cd is a minor isomorphic component (about 0.2%) (Forstner

1980). Small additional amounts of Cd are recovered during the processing of zinc-lead, zinc-copper and copper ores (Nriagu 1980). Specific natural Cd solids of interest include greenochkite and hawleyite, both diamorps of CdS, cadmoselite (CdSe), monteponite (CdO), otavite ($CdCO_3$), and Cd inclusions in natural apatite ores.

2.3 Uses of Cadmium

The most important uses of Cd are in alloys, in electroplating (automotive industry), in pigments, as stabilisers for polyvinyl plastics, and in batteries (Ni-Cd batteries). As an impurity in Zn, significant amounts of Cd are also present in galvanised metals. Cadmium is also used in photography, lithography, process engraving, rubber curing, and in fungicides. Consequently, Cd can be found in a wide variety of consumer goods, and virtually all households and industries have products that contain Cd.

Table 2.1 Cadmium concentrations in rocks (mg kg^{-1} or % where indicated) (*source* Alloway 1990)

	Range	Mean
Igneous rocks		
Rhyolites	0.03 - 0.57	0.23
Granites	0.01 - 1.60	0.20
Basalts	0.01 - 0.60	0.13
Metamorphic rocks		
Gneisses	0.007 - 0.26	0.04
Schists	0.005 - 0.87	0.02
Sedimentary rocks		
Shales and clays	0.017 - 11	-
Black shales	0.30 - 219.0	-
Sandstones and conglomerates	0.019 - 0.4	-
Carbonates	0.007 - 12	0.065
Phosphorites	<10 - 980	-
Coal	0.01 - 300	
Crude oil	0.01 - 2.1	
Sulphide ore minerals		
Sphalerite (ZnS)	0.2 - 0.4 (< 5 %)	
Galena (PbS)	< 0.5 %	
Tetrahedrite-tennartite (Cu.Zn) (Sb.As)S	< 0.24 %	
Metacinnabar (HgS)	< 11.7 %	

2.4 Cadmium and humans

Cadmium is unique among metals because of its diverse toxic effects, extremely protracted biological half-life (approximately 10 - 30 years in humans), low rate of excretion from the body, and predominant storage in soft tissues (primarily liver and kidney) rather than bone (Goering *et al.* 1995). No homeostatic mechanism has been found by which the amount of Cd in the body is regulated (Venugopal and Luckey 1978), and as a consequence, the amount of Cd in a human increases with age.

Cadmium poisoning was first definitively recognised in the 1920's, in people who had ingested acidic food stored in cadmium-lined containers (Schroeder 1974). Other health hazards associated with Cd exposure became known in the 1940's when Friberg (1948) reported the occurrence of emphysema and proteinuria in workers exposed to Cd dust. In the 1960s, Cd was thrown into the mainstream of metal toxicology research when Cd was identified as the major etiological factor in Itai-Itai disease, a condition that afflicted Japanese women exposed to Cd via their diet which contained Cd-contaminated rice (*Oryza sativa* L.) and water. Continued exposure to small amounts of Cd leads to accumulation as a metalloprotein cadmium-thionein, in human and animal liver and kidney tissue, resulting in damage and dysfunction to these organs (Webb 1975). Although chronic exposure to Cd has also been implicated in medical conditions such as emphysema, gastric and intestinal dysfunction, anaemia and essential hypertension (Lagerwerff 1972), the role of Cd as the major predisposing factor in these conditions is far from clear. The World Health Organisation (WHO) recommends a maximum Cd intake of 1μg Cd kg^{-1} body weight day^{-1} (WHO 1972).

2.5 Sources of cadmium in agricultural soils

Cadmium inputs into agricultural soils can come through three predominant pathways. These include atmospheric deposition, sewage sludge application and fertiliser application.

2.5.1 Atmospheric deposition

Cadmium can be deposited from the atmosphere onto soil and vegetation growing on them, however the amounts will vary and depend upon the distance from a point source of pollution. The major sources of atmospheric emissions are from high temperature

industrial processes such as non-ferrous metal production, coal and oil combustion, municipal and sewage sludge incineration, cement production and iron and steel production (Table 2.2). The significance of atmospheric inputs of Cd into a soil system can be assessed by comparing archived and contemporary soils of known history (Tjell and Christensen 1985; Jones *et al.* 1987). The importance of atmospheric inputs of Cd into soil was first brought to world attention following the work by Tjell *et al.* (1981) on Danish soils where a mass balance quantifying Cd inputs and outputs was undertaken. Subsequent work by Hovmand *et al.* (1983) showed that between 20 - 60 % of grassland foliar Cd at a rural site in Denmark was atmospherically derived. Singh (1991) indicated that in Norway, 14 - 65% of the Cd concentration in crops was due to atmospheric deposition. Merry and Tiller (1991) found atmospheric deposition of Cd accounted for up to 3 g ha^{-1} yr^{-1} in urban areas in Adelaide, South Australia. In the United States, values ranging from 1.4 g ha^{-1} yr^{-1} in remote areas, to 6.3 g ha^{-1} yr^{-1} in urban areas have been recorded, whereas recent monitoring in rural areas in the United Kingdom show mean atmospheric deposition of around 2.5 g ha^{-1} yr^{-1} (Alloway and Steinnes 1997).

Table 2.2 Estimated Cd atmospheric emissions from major sources in Europe in 1979 (tonnes yr^{-1}) (*Source* Pacyna 1987)

Primary non-ferrous metal production	1658
Coal combustion	146
Oil combustion	110
Refuse incineration	85
Iron and steel manufacture	60
Industrial applications of metals	20

2.5.2 Sewage sludge

Sewage sludge contains a wide range of Cd concentrations. Values ranging from <1 - 3650 mg kg^{-1} Cd dry matter having been reported in western Europe and North America. In New Zealand, land application of wastes is becoming more widespread as regulating authorities move to protect water quality by restricting waste disposal into rivers, lakes and the marine environment (Cameron *et al.* 1997). This may lead to a potential increase in Cd loading to the agricultural system and as a consequence many countries have recommended maximum annual Cd soil loadings from sewage sludge application Table 2.3.

Table 2.3 Current or proposed legislation regarding maximum permissible Cd concentrations (mg Cd kg^{-1}) in sludges applied to agricultural land (*source* OECD 1994)

Country	Sludge Cd concentration (mg Cd kg^{-1})	Limit on Cd loading to agricultural land (g ha^{-1})
Australia	3	-
Austria	5	25 y^{-1} (crops) 12.5 y^{-1} (pasture)
Canada	20	4000 over 45 years
Finland	-	3 y^{-1}
Germany	5-10 depending on soil	-
Netherlands	1.25	-
Norway	10	-
New Zealand	**15**	**200 y^{-1}**
Sweden	4	-
Switzerland	5	-
UK	-	150 over 10 years
USA	39	500

2.5.3 Fertiliser inputs

Numerous reports have documented an increase in soil Cd concentration as a result of phosphate fertiliser application (Williams and David 1973; Rothbaum *et al.* 1986; Merry 1988; Roberts *et al.* 1994). The Cd content of phosphate fertilisers varies depending upon the source of the raw rock phosphate used in its manufacture. Table 2.4 presents Cd concentrations for phosphate rocks used from around the world and indicate that the highest Cd concentrations in rock phosphates are recorded for deposits in North Carolina, Ocean Islands, Nauru and especially Western USA. Until recently, the main source of rock phosphate for phosphate fertiliser manufacture in New Zealand and Australia was from oceanic sedimentary and guano-based deposits with Cd concentrations between 34 - 69 mg kg^{-1} for New Zealand (Rothbaum *et al.* 1986) and 42 - 99 mg kg^{-1} for Australia (McLaughlin *et al.* 1996). Phosphate fertilisers are the most ubiquitous source of Cd contamination in agricultural soils of New Zealand and Australia, because in the manufacture of single superphosphate (SSP) almost all of the Cd present in the original phosphate rock is found in the final fertiliser (Williams 1977), as is 60 - 70% of the Cd in triple superphosphate (TSP) (Wakefield 1980). Regulation of maximum Cd concentrations in phosphatic fertiliser have been under consideration in a number of countries. Many countries have implemented maximum limits, while others have voluntary guidelines

(Table 2.5). The New Zealand fertiliser industry has a voluntary reduction policy for Cd, with the year 2000 limit of 280 mg Cd kg^{-1} already met. The concentration of Cd in other manufactured fertilisers e.g. nitrogenous or potassic fertilisers are generally low (Zarcinas and Nable 1992).

Table 2.4 Cadmium and phosphorus concentrations of some phosphate rocks

Phosphate rock	Cd (mg kg^{-1})	P (%)	Cd (mg Cd kg^{-1} P)	References
USSR (Kola)	0.2	17.2	1	Singh (1991)
South Africa (Phalaborwa)	4	17.2	23	Williams (1974)
Chatham Rise phosphorite	2	8.9	23	Syers *et al.* (1986)
China (Yunan)	5	14.4	35	Bramley (1990)
Jordan	6	14.8	27	Bramley (1990)
Australia (Duchess)	7	13.9	50	Williams (1974)
Mexico	8	14.0	57	Syers *et al.* (1986)
Egypt (Quseir)	8	12.7	61	McLaughlin (unpub.data)
Makatea	10	13.0	77	Syers *et al.* (1986)
Peru (Sechura)	11	13.1	84	Syers *et al.* (1986)
Israel (Arad)	12	14.1	85	Syers *et al.* (1986)
Tunisia (Gafsa)	38	13.4	108	Syers *et al.* (1986)
Israel (Zin)	32	14.0	228	Bramley (1990)
Morocco (Boucraa)	38	15.7	240	McLaughlin (unpub.data)
Christmas Island	43	15.3	275	David *et al.* (1978)
North Carolina	47	15.1	311	McLaughlin (unpub.data)
Banaba (Ocean Island)	99	17.6	563	Williams (1974)
Nauru	100	15.6	641	Syers *et al.* (1986)
Western USA	60 - 340	NR[A]	NR	Auer (1977)

[A] NR, not reported

2.5.3.1 Removal of Cd from fertiliser

Currently there is no feasible commercial process that exists for the elimination of Cd from phosphate rock or phosphoric acid (Ghoshesh *et al.* 1996). A number of methods are currently being investigated and evaluated at the 'laboratory bench' and 'pilot plant' level, which include solvent extraction techniques, ion-exchange, inorganic sulphide precipitation, and electrolysis. The disadvantages of all of the proposed practices is the likely associated increased costs of the final product.

Table 2.5 Current or proposed legislation regarding Cd concentrations (mg Cd kg^{-1} P) of fertilisers in New Zealand and in New Zealand's trading partners (Compiled from OECD 1994 and other sources)

Country	Cd level (mg Cd kg^{-1} P)
Austria	175
Denmark	110 from July 1995
France	none
Germany	90 voluntary
Japan	340
Netherlands	20
Norway	100
Sweden	Over 5 = tax of 30 SEK/mg Cd 100 maximum
Switzerland	50
UK	None
USA	None
Australia	
Tasmania	
Phosphatic fertilisers	450
Trace element fertilisers	80 (per kg product)
Soil Amendments	10 (per kg product)
Victoria (proposed)	
Phosphatic fertilisers	350
Other fertilisers	10 (per kg product)
New Zealand	420 from 1995 (voluntary) 340 from 1997 280 from 2000

2.6 Cadmium in soils

Cadmium concentrations in soils are variable, and comparison between countries is complicated given that firstly, it is often unclear if soil Cd concentrations quoted are for unfertilised (native) or fertilised (agricultural) sites, and secondly, to what depth soils have been sampled. Total Cd concentration values reported worldwide in "normal" agricultural soils vary from less than 0.01 mg kg^{-1} to over 2.50 mg kg^{-1}, but generally soils fall in the range less than 0.05 - 1.00 mg kg^{-1} (Table 2.6). For example, mean Cd concentrations for several European countries indicate that values range from 0.22 mg kg^{-1} in Sweden up to 1.20 mg kg^{-1} in England and Wales. Recently, Sillanpaa and Jansson (1992) published the results of a comprehensive worldwide study of Cd concentrations found in 3500 soils from

30 countries. They found the median concentration was approximately 0.05 mg kg^{-1}. They were however using a mild extractant (0.05 M AAAc-EDTA) that is used to measure the plant available fraction of Cd.

2.6.1 Cadmium in New Zealand soils

A recent national survey in New Zealand examining the Cd status of pastoral (fertilised) versus native (unfertilised) soil sites indicates that on average, total soil Cd concentrations at pastoral sites were double those at their native counterparts (Roberts *et al.* 1994). The fact that total soil Cd was highly correlated with total soil phosphorus (P), was taken as evidence that phosphatic fertilisers were the source of Cd enrichment in pastoral soils. In addition, the Zn:Cd ratio of pastoral soils compared to native soils decreased in all soil groups sampled.

Native soils typically had Zn:Cd ratios of c. 180:1 to 1120:1, whereas the pastoral soils had ratios ranging from c. 70:1 to 630:1. A decrease in the Zn:Cd ratio was attributed to addition of Cd contained in P fertiliser such as superphosphate, which has a Zn:Cd ratio of 23:1 or less. The average total Cd concentration in pastoral soils (0 - 7.5 cm) was 0.44 mg kg^{-1} range (0.04 - 1.53 mg kg^{-1}) while the mean Cd concentration in native sites was 0.20 mg kg^{-1} range (0.02 - 0.77 mg kg^{-1}). Similarly, McIntosh *et al.* (1997) found that total Cd concentrations for three New Zealand soil groups (Pallic, Brown and Melanic) on farmland soils, which has received regular fertiliser application, were significantly higher than Cd concentrations on reserve soils. The mean total Cd concentration of New Zealand soils fall at the lower end of the range compared to other countries (Table 2.6).

Table 2.6 Total cadmium (Cd) content of soils from around the world

Country	Soil	Sampling depth	Cd mean (mg kg^{-1})	Cd range (mg kg^{-1})	Reference
Sweden	Agricultural	0 - 20	0.22	0.03 - 2.30	Andersson (1977)
Denmark	Agricultural	0 - 20	0.25	0.03 - 0.90	Tjell & Hovmand (1978)
Netherlands	Agricultural	0 - 20	0.40	0.21 - 0.59	De Boo (1978)
Australia	Agricultural	0 - 10	0.13	0.03 - 0.32	Williams & David (1973)
England & Wales	Rural	0 - 15	1.20	0.01 - 4.10	McGrath (1986)
Canada	Agricultural	0 - 15	0.56	0.10 - 8.10	Frank *et al.* (1976)
United States	Agricultural	0 - 20	0.13	0.03 - 0.32	Holmgren *et al.* (1993)
New Zealand	Native	0 - 7.5	0.20	0.02 - 0.77	Roberts *et al.* (1994)
New Zealand	Pastoral	0 - 7.5	0.44	0.04 - 1.53	Roberts *et al.* (1994)

2.6.2 Long-term accumulation of Cd in soils

Cadmium accumulation in agricultural soils due to the long-term use of phosphate fertilisers has been recognised in several studies from a number of countries (Mordvedt *et al.* 1981; Singh 1991). Baerug and Singh (1990) for example showed that long-term use of commercial fertilisers increased the Cd concentration of soils in three regions of Norway. Semu and Singh (1996) studied the accumulation of heavy metals in soils and plants in Tanzania after the long-term use of fertilisers. They conclude that high total and extractable Cd concentrations in soil from the high fertilised sites compared to native sites was caused by the long term use of P fertilisers. Mulla *et al.* (1980) showed that the concentration of Cd in a surface soil treated with broadcast phosphate fertiliser for 36 years averaged 1 mg Cd kg^{-1} as compared to 0.07 mg kg^{-1} in the control. The concentration of Cd in the surface soil was highly correlated with the total soil P. Rothbaum *et al.* (1986) investigated Cd accumulation on a permanent grassland site at Rothamsted, England which had received phosphate fertiliser for 100 years. Results indicated that there was an increase in total soil Cd concentration from 0.17 mg kg^{-1} to 0.44 mg kg^{-1} during this period. When atmospheric Cd inputs are removed, the annual rate of increase in soil Cd amounts to at least 4 g ha^{-1} yr^{-1}. Rothbaum *et al.* (1986) also sampled soil from a 30 year old grassland experiment in New Zealand, where Cd had been derived from superphosphate additions. Cadmium concentrations in control (native) plots were 0.23 mg kg^{-1} in the 0-5 cm layer, whereas they were 0.49 mg kg^{-1} in the fertilised plots. Also in New Zealand, Loganathan *et al.* (1995) studied the Cd distribution in hill pasture soils which had 20 years of phosphate fertiliser application. The average total Cd concentration in the surface soil which had received 425 kg of (SSP) ha^{-1} yr^{-1} was 0.44 mg kg^{-1} , compared to 0.1 mg kg^{-1} for the control.

2.7 Forms of soil Cd

2.7.1 Cadmium in soil solution

Soil solution Cd is the central focus of soil Cd chemistry since that is the predominant medium from which plants absorb Cd and other nutrients, and is the centre of all important soil chemical processes (Lindsay 1979).

Numerous studies have indicated that the dominant Cd species present in soil solutions of agricultural soils or sludge amended soils is the free Cd^{2+} ion or Cd complexed by inorganic ligands (Mahler *et al.* 1980; Tills and Alloway 1983; Holm *et al.* 1993; Naidu *et al.* 1994). After release into soil solution, either from dissolution from fertiliser or sewage sludge, the free Cd ion (Cd^{2+}) is rapidly partitioned between the mineral, organic and solution phases. This is influenced by the properties of the soil and composition of the soil solution, which determine the dynamic equilibrium between trace metals in solution and the soil-solid phase. A model of the possible reactions that can affect the soil solution concentration of free Cd ions in a soil system is shown in (Figure 2.1). The free ion is selected as the central species, given that this is the form of Cd available for plant uptake. The concentration of Cd^{2+} in soil solution is affected by a number of soil reactions, including ion exchange, solubility phenomena, sorption/desorption processes, complexation and redox reactions (Figure 2.1). In solution, Cd^{2+}, like some of the other metal ions is associated with a sheath of water molecules. The aquo ion is a strong Lewis acid which in the presence of moisture can dissociate a proton:

$$Cd(H_2O)_6^{2+}(aq) \rightleftharpoons Cd(H_2O)_5(OH)^{+} + (aq) + H^{+} \quad (pH*1 = 10.1)$$

Cadmium, a strong Lewis acid, reacts and forms complexes most readily with soft Lewis bases (Puls and Bohn 1988), the most important being inorganic ligands (Table 2.7) such as Cl^-, SO_4^{2-}, HCO_3^- or various organic ligands. The effect of ligands on Cd sorption will be discussed further in section 2.9.5.

Table 2.7 Equilibrium association constants of Cd with selected inorganic anions (*source* Lindsay 1979)

ligand	complex	log K^o
Cl^-	$CdCl^+$	1.98
	$CdCl_2^0$	2.60
	$CdCl_3^-$	2.40
SO_4^{2-}	$CdSO_4^0$	2.45
NO_3^-	$CdNO_3^+$	0.31
	$Cd(NO_3)_2^0$	0.00
$H_2PO_4^-$	$CdHPO_4^0$	-4.00
HCO_3^-	$CdHCO_3^+$	-5.73
	$CdCO_3^0$	-14.06
OH^-	$CdOH^+$	-10.10
	$Cd(OH)_2^0$	-20.30

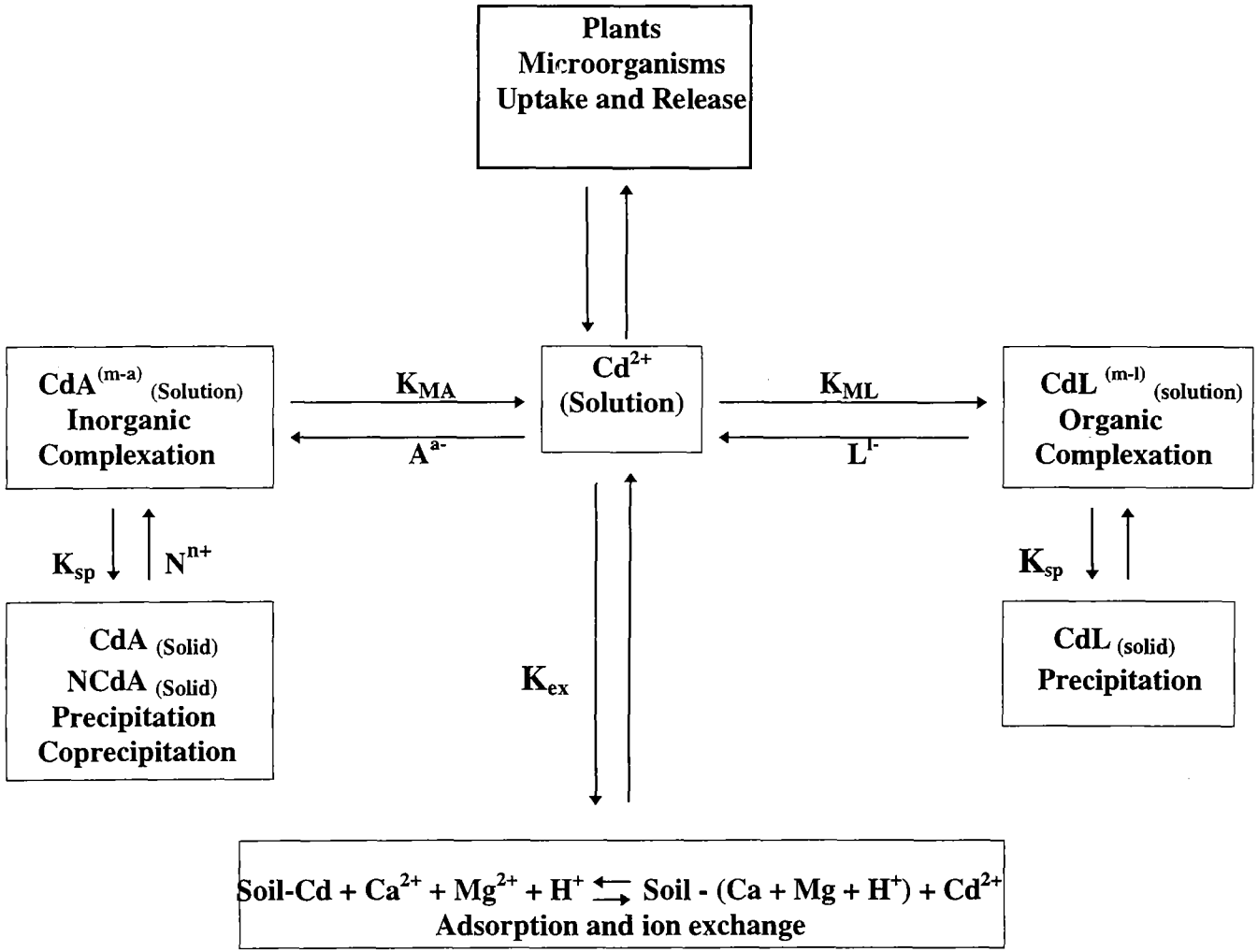

Figure 2.1 Possible reactions that affect the free ion concentration of Cd in the soil-water system. (Adapted from Helmke and Naidu 1996).

2.7.2 Cadmium associated with the soil solid phase

As discussed above, Cd can occur in soils in the soil solution, however this is only a small proportion of the total soil Cd. Most soil Cd is associated with the soild phase, sorbed onto hydrous oxides of Mn, Fe, and Al as insoluble organometal complexes, as solid phase insoluble precipitates, and in solid phase minerals (Fig 2.1). Chemical fractionation techniques have been used extensively to fractionate heavy metals such as Cd in soils, in an attempt to identify these associations (Tessier *et al.* 1979; Shuman 1985; Mann and Ritchie 1993; Ramos *et al.* 1994). Chemical fractionation can provide very useful information about a metal's chemical distribution within a soil, its bioavailability, an indication of the soil as a medium for storing metals, and its leaching potential (Keller and Vedy 1994). Many different fractionation schemes have been described in the literature, each with its potential advantages and disadvantages (Beckett 1989). As yet, no single scheme has been universally accepted for metal fractionation in soils. The schemes described by Tessier *et al.* (1979) and Shuman (1985) (sometimes with modifications) are used quite frequently. In Europe, attempts have been made to standardise metal fractionations using a procedure described by Quevauviller *et al.* (1994). Fractionation schemes often differ in detail and reagents used e.g. pH, temperature, strength of extractant, soil:solution ratios and extraction time (Beckett 1989). This has complicated comparison of results from one study to another (Lake *et al.* 1984). Generally 3 - 8 extraction steps have been used, starting with the least aggressive reagent and progressing through to more destructive extractants (Beckett 1989). However generally, most chemical fractionation schemes fractionate Cd into exchangeable, organic, oxide and residue fractions.

Berti and Jacobs (1996) highlighted the fact that comparison of fractionation data between studies is often complicated, given that very differing soils are used e.g. native versus sludge or salt amended soils and also very different sequential fractionation techniques are employed. Krishamurti *et al.* (1995a) used a fractionation scheme to investigate native Cd in 16 surface soils from Saskatchewan. Krishamurti *et al.* (1995a) found that exchangeable Cd was negligible using 1M $Mg(NO_3)_2$, while Cd in the amorphous and crystalline oxide fractions were significantly lower than organic and residual fractions in the soils investigated. Krishamurti *et al.* (1995a) showed that Cd was predominantly in the form of metal-organic complexes, which accounted for on average, 40% of the total Cd

present. Chang *et al.* (1984), who studied the chemical forms of heavy metals in sludge treated soils by sequential fractionation, also found that Cd associated with the exchangeable and adsorbed fractions were negligible, while Cd was mainly in carbonate and residual forms in the soils studied. By contrast, Hickey and Kittrick (1984) found the greatest concentrations of Cd were in the first fraction (1M $MgCl_2$, pH 7) in soils containing high levels of heavy metals. In a study by Emmerich *et al.* (1982), Cd was mostly found in the 4th fraction (0.05 Na-EDTA), whereas, Berti and Jacobs (1996) found that soils amended with sludge containing up to 2.2 μg Cd g^{-1}, could only detect Cd in the exchangeable (0.5M $Ca(NO_3)_2$ and acid soluble (0.44M CH_3COOH + 0.1M $Ca(NO_3)_2$) fractions.

2.8 Sorption of Cd by soils

Tiller *et al.* (1984a) and Swift and McLaren (1991) indicate that trace metal concentrations in soil solution are likely controlled by sorption/desorption equilibria at low metal concentrations. Precipitation-dissolution reactions only become important at high metal loadings where precipitates of Cd phosphates and carbonates may form (Santillan-Medrano and Jurinak 1975; Street *et al.* 1977).

According to Sposito (1984), trace metal sorption processes in soils can be separated into two groups, depending on the affinity of the adsorbent for the adsorbate. If no molecule of the bathing solvent is interposed between the surface functional group and the molecular unit it links, the complex formed is called an *inner-sphere complex.* This type of complex involves covalent and ionic bonding and is termed 'specific sorption'. If at least one solvent molecule is interposed between the functional group and the bound molecule, the complex formed is called an *outer-sphere complex.* This type of complex involves less stable electrostatic bonds and is termed 'nonspecific sorption'. Sorption of trace metals in soils takes place in the presence of solution concentrations of major cations, which are orders of magnitude higher than those of the trace metals. Under these conditions, as a result of mass action, sorption of trace metals by normal ion exchange reactions, forming outer-sphere complexes is negligible (Swift and McLaren 1991). Therefore sorption of trace metals, such as Cd, by soil and soil components is considered to be due predominantly to specific sorption, or *inner-sphere* mechanisms.

Sorption isotherms have been plotted for Cd by numerous workers using many differing soil types. Cadmium sorption data have been fitted to Linear equations (Garcia-Miragaya and Page 1978; Petruzzelli *et al.* 1985; Kim and Fergusson 1992; Boekhold *et al.* 1993) to Freundlich equations (O'Connor *et al.* 1984; Chardon 1984; Christensen 1984a; Kookana *et al.* 1994; Bajracharya *et al.* 1996) and Langmuir equations (Cavallaro and McBride 1978; Navrot *et al.* 1978).

Linear sorption isotherms have been noted by a number of workers investigating Cd sorption at low concentrations. The linearity is indicative of a constant partition coefficient between the soil and the solute, and this is often the case at low solution concentrations. Sposito (1984) describes this type of adsorption isotherm as a C-curve isotherm, where the initial slope remains independent of adsorptive concentration (Figure 2.2). Often comparison of sorption between soils is achieved by comparing the sorption gradients i.e K_d values, which is the Cd distribution coefficient expressing the ratio of sorbed Cd to solution Cd at equilibrium. Jarvis and Jones (1980), O'Connor *et al.* (1984) and Alloway *et al.* (1985) investigated Cd sorption and showed that sorption could be described by a two part Freundlich isotherm that represents Cd retention by highly specific sorption sites at lower concentrations and a mixture of specific and non-specific sorption at higher concentrations. Data fitted to Langmuir sorption isotherms often involves high equilibrium solution concentrations which are not often relevant to Cd concentrations found in soils.

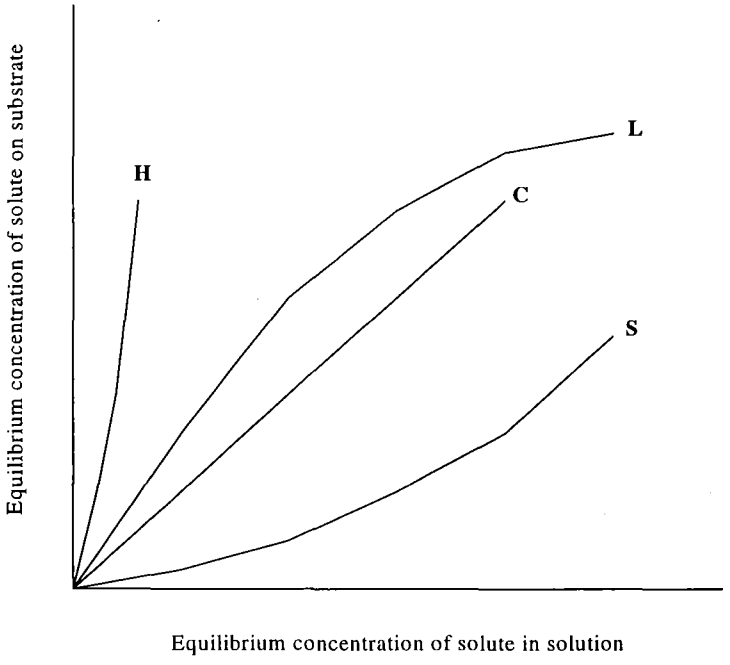

Figure 2.2 Four classes of sorption isotherms as descirbed by Giles *et al.* (1974).

2.8.1 Sorption by soil components

The soil is a complex heterogeneous system that is composed of a mixture of reacting surfaces. The reactive surfaces involved in the sorption behaviour of soils can be conveniently grouped into three categories: layer silicate clays, organic matter and metal oxides (e.g. Fe, Al, and Mn). Numerous investigations have studied sorption of Cd onto individual soil components such as clay minerals (Garcia-Miragaya and Page 1976; Tiller *et al.* 1979; Tiller *et al.* 1984a; Garcia-Miragaya *et al.* 1986; Spark *et al.* 1995a; Zachara and Smith 1994) organic matter (McBride *et al.* 1981; Gerritse and Van Driel 1984; Elliott *et al.* 1986; Kuo 1990) and metal oxides (Kuo and McNeal 1984; Tiller *et al.* 1984b; Ainsworth *et al.* 1994; Backes *et al.* 1995; Spark *et al.* 1995b).

2.8.1.1 Layer silicate clays

Layer silicate clays exhibit permanent charge usually generated by isomorphous substitution of ions within the clay lattice. Some variable charge sites are also found at the

fractured edges of lattices and these vary as a proportion of the total clay charge depending upon the nature of the clay mineral and its particle size. The importance of clay in the determination of soil Cd adsorption characteristics has been highlighted by a number of workers (Garcia-Miragaya and Page 1976; Farrah and Pickering 1977; Reid and McDuffie 1981).

Zachara and Smith (1994) showed Cd sorption on smectite was a combination of ion exchange on fixed-charge sites and surface complexation to hydroxylated edge sites. Furthermore, edge site sorption appeared to be dominated by Cd complexation to broken bond AlOH sites. Inskeeps and Bahan (1983) found Cd sorption onto montmorillonite was not as pH dependent as metal sorption on oxide surfaces or clays where interlayer surface area is negligible. These authors indicated that constant potential edge sites at low sorption density were also responsible for Cd sorption. Puls *et al.* (1991) investigated the effects of pH, solid/solution ratio, ionic strength, and organic acids on Pb and Cd sorption on kaolinite. Results showed that as pH increases, the kaolinite edge sites become more negatively charged and sorption increases, and they indicate that decreased Cd sorption with increased Na^+ competition indicated ion-exchange mechanisms control metal sorption by kaolinite. Sparks *et al.* (1995a) also studied trace metal adsorption onto kaolinite. They concluded that sorption of Cd^{2+} onto kaolinite occurred by two distinct processes. Type 1 involved permanent charges on kaolinite faces, whereas type 2 is associated with variable-charge surfaces. In a study by Garcia-Miragaya *et al.* (1986), it was discovered that the preference of kaolinite above montmorillonite for Cd at low metal loading was a result of the relatively greater concentration of weakly acidic edge sites (especially AlOH groups) on kaolinite. However at higher Cd loadings, permanent charge sites (low affinity sites) became more important. Ziper *et al.* (1988) investigated Cd sorption onto a range of clay minerals, and concluded that highly selective adsorption of Cd occurred on edge sites, and the contribution of external planar and interlayer surfaces was not appreciable.

2.8.1.2 Organic matter

Organic matter has a high negative charge density, arising mainly from the dissociation of carboxyl and phenolic groups. This results in the net charge on the soil colloids becoming increasingly negative as the soil pH values increase. Metals can react with soil organic

matter by ion exchange, complexation, and precipitation reactions. Indications by Stevenson (1982) are that carboxyl groups are the group of most importance in Cd sorption on organic matter, with Cd forming inner sphere complexes with dissociated functional groups. The extent of retention of metals by soil organic matter at pH 5.8 decreases in the order Fe = Al = Cr = Hg = Pb = Cu > **Cd** > Zn > Ni > Co > Mn (Schnitzer and Khan 1978).

Lee *et al.* (1996b) investigated the sorption of Cd on 15 soils, and found Cd sorption was highly pH dependent, however among all soil properties investigated, organic matter was the most important in controlling sorption. Riffaldi and Levi-Minzi (1975) found an increase in Cd sorption onto humic acid with a rise in pH. Kim and Fergusson (1992) identified that the organic component in the soil they studied was extremely important in controlling Cd sorption. Taylor and Theng (1995) showed that complexes of kaolinite with humic acid had a greater propensity for sorbing Cd than clay alone. The amount of Cd sorbed was related specifically to the concentration of ionised carboxyl groups.

2.8.1.3 Metal oxides

Oxides and hydroxides of Al, Fe and Mn are a group of soil colloids that are important sorbents for a number of trace metals, including Cd, whose sorption to and desorption from the surface of oxides influence sorbate behaviour in the environment (Ainsworth *et al.* 1994). Oxide and hydrous oxides exhibit pH dependent variable charge generated by protonation and deprotonation of surface oxygens and hydroxyl groups. These mechanisms not only determine the surface potential of oxides, but are involved in the processes of inner sphere, specific adsorption of ions, including Cd. Sorption onto oxides can occur even at pH levels below the oxide point of zero charge (pHzpc), thus overcoming electrostatic repulsion (Chubin and Street 1981). Sorption of Cd often increases sharply as pH increases, resulting in a characteristic S-shaped curve (pH sorption edge). Garcia-Miragaya and Page (1978) showed that at pHs between 6.0 and 7.0, iron oxides have a higher affinity for trace amounts of Cd than do 2:1 layer silicates. Zasoski and Burau (1988) showed that 2 or more mechanisms or sites of sorption for both Zn and Cd on a hydrous manganese oxide. Higher energy sites showed preference for Cd over Zn. High energy binding is an exchange sorption on the negatively charged oxide sites by displacement of surface and diffuse layer cations and protons. Tiller *et al.* (1984b) showed

that sorption of metals, including Cd onto oxides appear to be controlled by mechanisms involving metal-ion hydrolysis.

2.9 Factors affecting Cd sorption by soil constituents

2.9.1 pH

Soil pH has a marked effect on the sorption of Cd. There are numerous studies showing that with increasing soil pH, there are dramatic increases in Cd sorption onto minerals and soils (Garcia-Miragaya and Page 1978; Christensen 1984a; Gerritse and Van Driel 1984; Boekhold *et al.* 1993; Naidu *et al.* 1994; Taylor and Theng 1995). With increasing pH, there is a characteristic pH above which sorption of Cd increases rapidly (Gerritse and Van Driel 1984; Zachara *et al.* 1992; Naidu *et al.* 1994;). Generally sorption increases from <20 - 100% within the narrow pH range 3-5, as previously mentioned, called the adsorption edge (Naidu *et al.* 1994).

Boekhold *et al.* (1993) found for each 0.5 unit increase in pH resulted in twice as much sorption onto an acid sandy soil. Garcia-Miragaya and Page (1978) showed in their study, that in general there was a decrease in the amount of Cd sorbed as pH decreased. They stated this was expected given increasing concentrations of H^+ and Al^{3+} ions in solution both which compete with Cd for ion sorption sites on soil sorbent surfaces. Christensen (1984a) showed that Cd adsorption by sandy and loamy soils increased by a factor of three for every pH unit increase between 4 and 7.7. Various models have been suggested to describe the sorption mechanisms involving metal ions:

(i) The metal hydrolysis model (Hodgson *et al.* 1964), where hydrolysis of metal ions results in formation of metal hydoxy species which are sorbed preferentially over the metal ion;

(ii) The metal proton exchange model (Boekhold *et al.* 1993), which assumes Cd and H^+ are sorbed onto the same sites in soils;

(iii) pH-dependent ion-exchange model based on electrostatic potential on the plane of adsorption and surface-charge density (Naidu *et al.* 1994). Essentially the electrostatic potential on variable charged surfaces decreases with increasing pH, thus making the surface more negative (Barrow 1984).

2.9.2 Ionic strength

A number of studies have identified that with increasing ionic strength, there is a concomitant decrease in sorption of Cd onto individual soil minerals and whole soils (Garcia-Miragaya and Page 1976; Gerritse and Van Driel 1984; O'Connor *et al.* 1984; Petruzzelli *et al.* 1985; Puls *et al.* 1991; Boekhold *et al.* 1993). The effect of ionic strength on metal sorption has often been attributed to:

(i) Change in the activity of free Cd^{2+} and $Cd(OH)^{+}$ due to ion-pair formation (Garcia-Miragaya and Page 1976);
(ii) Effect of ionic strength on pH;
(iii) Competition for the sorption sites on soil surfaces (Homann and Zasoski 1987);
(iv) Changes in electrostatic potential in the plane of sorption (Barrow 1986).

Petruzzelli *et al.* (1985) suggests that ion-pair formation of Cd^{2+} with Cl^- anions in their study must be taken into account for sorption decreases with increased ionic strength. The index anion (Cl^-) forming negatively or neutral species. Garcia-Miragaya and Page (1976) attributed reduced sorption of Cd^{2+} to montmorillonite in a background of $CaCl_2$ to the presence of uncharged and negatively charged complexes of Cd^{2+} with Cl^- ligands. Many studies attribute reduced Cd sorption with increasing ionic strength to greater competition for sorption sites between Cd and the index cation in the background electrolyte (Garcia-Miragaya and Page 1976; Homann and Zasoski 1987; Zhu and Alva 1993).

Naidu *et al.* (1994) state that the effects of ionic strength on metal sorption are dependent on the surface properties of the soil particles. In their study, the sorption of Cd increased with increasing ionic strength in an Oxisol at pH values below the point of zero charge (PZC), but it decreased with ionic strength in soils with a net negative charge. Bearing in mind that increasing ionic strength always decreases cation sorption above the PZC, it has been suggested that the effects of ionic strength on sorption operates through its effects on electrostatic potential in the plane of sorption rather than through its effect on surface charge (Naidu *et al.* 1994). Thus if increasing ionic strength decreases cation sorption, then the potential in the plane of sorption is negative. If increasing ionic strength increases sorption below the PZC, then potential in the plane of sorption is positive.

2.9.3 Concentration of Cd

Sorption isotherms at low Cd^{2+} concentration differ from those at high Cd^{2+} concentration, with the affinity of Cd for soil surfaces decreasing as the surface coverage increases (Hendrickson and Corey 1981). Christensen (1989) comments that in some studies investigating Cd sorption, (e.g. Levi-Minzi *et al.* 1976; McBride *et al.* 1981) concentrations of up to 500 mg kg^{-1} have been employed, which can correspond to 5 to 20 % of a soils CEC value. Such loadings are more likely to resemble ion exchange from moderate binding energy sites, which will be very different from sorption at low Cd concentrations more typically found in soils.

2.9.4 Competing ions

The sorption of Cd by soils is a competitive process. The degree to which Cd is sorbed is dependent upon the concentrations and identity of other cations in the system (Helmke and Naidu 1996). The presence of certain divalent cations (e.g. Ca^{2+}, Co^{2+}, Cu^{2+}, Pb^{2+}, Zn^{2+}) has been shown to retard the sorption of Cd by soils due to competition between Cd and the other metal ions (Zasoski 1974; Homann and Zasoski 1987). Christensen (1987) studying 12 Danish soils, found that mixtures of Ni, Co and Zn and Cr, Cu and Pb had inhibitory effects on Cd sorption, with Zn being the most important. Naidu *et al.* (1994) showed that increasing Ca concentration in a background electrolyte from 10^{-3} to 10^{-2} M in a sandy loam soil reduced sorption by 67%. This phenomena has been documented by other workers (Cavallaro and McBride 1978; Tiller *et al.* 1979). Bittel and Miller (1974) found Pb competed with Cd for sorption on a variety of clay minerals.

2.9.5 Ligand complexation

Ligands play important roles in numerous soil chemical processes. They comprise inorganic ligands such as (Cl^-), (SO_4^{2-}), (PO_4^{3-}) and (NO_3^-), Table 2.7, and organic ligands arising from both plant root exudates and decomposing plant residues. Chloride generally reduces Cd sorption by soil, and has been identified as increasing the mobility of Cd through soils (Garcia-Miragaya and Page 1976; Doner 1978; Boekhold *et al.* 1993). The ligand ion concentrations modify both the nature of the metal species in soil solution and interactions with soil particles. Garcia-Miragaya and Page (1976) showed the sorption of Cd^{2+} from Cl^- solutions diminished with increasing salt concentration concomitant with the

formation of uncharged ($CdCl_2^0$) and negatively charged complexes ($CdCl^{3-}$, $CdCl_4^{2-}$ etc.) of Cd with Cl^- ligands.

The influence of ligand ions on the reactions of Cd are complex and soil type dependent. A study by Garcia-Miragaya and Page (1976) found an increase of SO_4^{2-} concentrations in solution reduced Cd sorption onto soil as did Benjamin and Leckie (1982) for sorption by amorphous iron oxides, silica and gibbsite, but there was no effect of SO_4^{2-} on Cd sorption by lepidocrocite. Whereas Hoins *et al.* (1993) found increasing concentrations of SO_4^{2-} in solution resulted in greater sorption by goethite. Naidu *et al.* (1994) found that specific interactions of SO_4^{2-}, and PO_4^{3-} ions with strongly weathered soils may increase the negative charge on soil surfaces and enhance sorption of Cd, whereas the formation of metal-SO_4^{2-} complexes in soil solution may decrease sorption. Organic ligands can also influence sorption of Cd by soils. Elliott and Denneny (1982) showed that, among several organic compounds tested, the ability to reduce Cd retention by soil followed the order EDTA>NTA>oxalate=acetate. Farrah and Pickering (1977) similarly found that EDTA prevented the adsorption of Cd over the pH range 3 - 11. In a study by Neil and Sposito (1986), it was found that Cd sorption in soils amended with sewage sludge was inhibited by the formation of complexes of Cd with soluble organic ligands at low Cd concentrations.

2.9.6 Contact time

Some studies have indicated the rapid sorption of metals onto soil surfaces after exposure, with little or no change with contact time (Sidle and Kardos 1977; Christensen 1984a; King 1988). However in other work involving sorption of metals onto soils or soil components, increasing the contact time between soil and sorbed trace metal has lead to decreases in the metal's subsequent ability to desorb from the soil (Padmanabham 1983; McLaren *et al.* 1986; Hogg *et al.* 1993; Ainsworth *et al.* 1994; Backes *et al.* 1995; Fischer *et al.* 1996). Many soil chemical processes are time dependent. An important factor in controlling the rate of many soil chemical sorption/desorption reactions is the type and quantity of soil components. The type of surface complex such as outer sphere versus inner-sphere also affects rate and reversibility of sorption reactions. Outer-sphere complexation is usually rapid and reversible, whereas inner-sphere is slower and may appear to be irreversible.

Kinetics of metal sorption reactions on soils and soil components are often characterised by a rapid, followed by a slow reaction. For example, Bruemmer *et al.* (1988) studying Cd sorption onto goethite found a 21% increase in sorption as reaction time increased from 2h to 42 days. They attributed the slow kinetics to diffusion-controlled reactions on external and internal surface sites. Ainsworth *et al.* (1994) studied sorption of Cd^{2+} on hydrous ferric oxide (HFO) as a function of oxide aging and metal-oxide residence time. Aging the oxide with Cd^{2+} resulted in desorption hysteresis. For example, after 16 weeks, 20% of Cd added could not be desorbed, which was attributed to Cd being incorporated into a recrystallising solid via isomorphic substitution. Backes *et al.* (1995) found that when the initial sorption period for Cd on oxides of Fe and Mn was increased from 1 to 15 weeks, there was a substantial decrease in the proportion of sorbed Cd that could be subsequently desorbed form goethite in particular, with a similar but smaller effect observed for Mn oxides. Christensen (1984b) examined the effects of soil aging, where Cd was added to 2 soils, a sandy loam and a loamy sand, and then left for a period of up to 67 weeks before being subject to desorption. Christensen (1984b) found no evidence of stronger bonds developing within this contact time and Cd sorption was found to be completely reversible. Fischer *et al.* (1996) examining the micro-topography of goethite particles found numerous wedge-shaped micropores occurred at domain boundaries on this crystal. Fischer *et al.* (1996) suggest these micropores could affect adsorption and desorption of heavy metal ions where diffusion into extremely small pores of ions results in declining metal desorption potential with time.

2.9.7 Cation Exchange Capacity (CEC)

Several investigations have identified soil CEC as an important factor in the sorption of Cd by soils. Levi-Minzi *et al.* (1976) found that CEC along with organic matter correlated well with sorption parameters. Kuo and Baker (1980) concluded that pH, CEC and organic matter influenced sorption. He and Singh (1993b) and Haghiri (1974) found that decreased plant Cd concentrations as a result of organic matter additions to soil was predominantly due to the effect of an increase in soil CEC. A criticism raised by Christensen (1989) however was that in many of the studies where Cd sorption has been related to CEC, the Cd concentrations used have been excessive, with the sorption processes likely resembling

ion exchange by moderate binding sites which may not reflect the situation in a uncontaminated soil environment.

2.10 Desorption

Swift and McLaren (1991) indicate that compared to adsorption of micronutrients by soils and soil components, there has been comparatively few investigations concerned with desorption of micronutrients. This is especially true for Cd. Desorption processes are as important as sorption given that it is the desorption process which controls the amount and rate of release of contaminants, e.g. Cd for plant uptake. The effectiveness of the soil as a permanent sink for metal ions like Cd, depends on the number of high affinity sites (specifically sorbed Cd) and the reversibility of the reactions with them (Tiller *et al.* 1979). The few reports in the literature on Cd adsorption-desorption in soils, show that sorption is reversible in some cases but not in others.

O'Connor *et al.* (1984) investigated sorption/desorption of Cd by three calcareous soils, and found that sorption could be described by a two part Freundlich isotherm that represents Cd retention by highly specific sorption sites at lower concentrations and a mixture of specific and non-specific sorption at higher concentrations. Desorption data indicated that Cd was irreversibly sorbed at highly Cd-specific sites, but at higher Cd loading, the desorption mechanism becomes active. Sakurai and Huang (1996) studied Cd sorption and desorption on montmorillonite (Mt), hydroxyaluminium (HyA-Mt), and a synthetic hydroxyaluminium (HAS-Mt). It was found that the greatest desorption of Cd occurred from Mt, which is dominated by permanent negative charges, as indicated by the lack of specific sorption. On the other hand, HyA-Mt and HAS-Mt complexes contained intercalated material, which had some variable charge characteristics, containing specifically sorbed Cd, and made desorption difficult. Sakurai and Huang (1996) conclude that the number of ion exchange sites, expressed in terms of CEC, could not account for differences in the sorption/desorption phenomena of Cd ions on negatively charged sites on a clay colloid. Kookana *et al.* (1997) recently investigated Cd desorption and showed that the extent of desorption of Cd from soils is dependent on the relative affinity with which it is initially sorbed. Significant relationships between soil K_d values, and the amount of Cd desorbed from the soil were obtained. Tiller *et al.* (1984a) found that easily releasable

fractions (nonspecifically sorbed) of Cd and Zn were much higher in clay fractions from an Oxisol relative to those from highly negatively charged smectite dominant Xeralfs and Xerets. The trend was reversed at high pH, and Tiller *et al.* (1984a) comment that soil affinity and site saturation play a significant role in desorption.

Christensen (1984b) studied desorption of Cd from two soils (loamy sand, sandy loam) exposed to low Cd concentrations. Results showed reversibility of Cd sorption for both soils, indicating that the soils used were not permanent sinks for Cd. Similarly, Puls *et al.* (1991) showed that Cd exhibited complete reversibility of sorption on to a kaolinite clay mineral when subject to repeated washing in 0.01 M $NaClO_4$ at pH 6.0. Comans (1987) investigated sorption and desorption of Cd on illite clay at low Cd concentrations and ionic strength. Results again demonstrated complete reversibility of Cd sorption on illite, however long equilibrium times (7 - 8 weeks) were shown to be essential because of slow desorption kinetics.

In some cases desorption of Cd is completely reversible, and in other investigations there are some hysteresis effects. It appears that desorption of Cd is related to the types of sorption components in the soil, which governs how strongly Cd is bound to the soil and soil factors such as pH, sorption site saturation and contact time.

2.11 Factors affecting the plant availability of soil cadmium

Cadmium is taken up by plants predominantly as free uncomplexed Cd^{2+} from soil solution. The amount plants absorb depends on a combination of soil and plant factors which control the concentration (or activity) of Cd^{2+} in soil solution. Table 2.8 summarises some of the factors which affect plant Cd concentrations.

2.11.1 Soil pH

Soil pH is often regarded as the major variable controlling plant uptake of Cd from soils (Chaney and Hornick 1978). The effect of pH on Cd availability in soils is a function of the effect of pH on retention of Cd by soil surfaces. There have been numerous studies involving glasshouse and field trial experiments showing the effect pH has on plant uptake (MacLean 1976; Street *et al.* 1978; Eriksson 1989; Xue and Harrison 1991). Andersson

and Nilsson (1974) studied the effect of pH on Cd uptake by fodder rape (*Brassica napus* L.) and found that an increase in soil pH from lime application decreased Cd concentration in this crop. Similarly Han and Lee (1996) showed Cd uptake in radishes (*Raphanus sativus* L.) was significantly decreased by liming.

Table 2.8 Factors affecting cadmium uptake by plants from soil (*adapted from* Chaney and Hornick 1978)

Factors	Effects on cadmium uptake by plants
Soil	
1. pH	uptake increases as pH decreases
2. soil salinity	uptake increases with salinity
3. amount of cadmium present	uptake increases with concentration increases
4. metal sorption by soil	
	organic matter
	cation exchange capacity
	clay, Fe, and Mn oxides
micronutrients	e.g. zinc deficiency increases uptake
macronutrients	may increase or decrease uptake
temperature	higher temperature increase uptake
crop rotation	
temperature	
redox	
Crop	
1. species and cultivar	leafy vegs. > root vegs. >cereals > fruits
2. plant tissue	leaf > grain , fruit and edible root
3. leaf age	older > younger
4. metal interactions	presence of zinc reduces uptake of Cd

Guttormsen *et al.* (1995) examined the effect of soil pH on Cd uptake by cabbage (*Brassica oleracea* L.) and carrot (*Daucus carota* L.) over 3 years in a field experiment. Cadmium concentrations in cabbage and carrot were 23 and 46 % higher at pH 5.5, than at pH 6.5. In another field trial involving sludge treated soils, Hooda and Alloway (1997) showed that liming substantially decreased metal contents of carrots and spinach (*Spinacia oleracea* L.), however the effect of liming had no substantial effect on content of wheat. In contrast, other studies have shown that concentrations of Cd in plants have been unaffected by changes in soil pH or in fact resulted in increases in Cd uptake. Andersson and Siman (1991) did not find a consistent pH effect in a study of nine locations in long-term limestone and fertiliser trials. Similarly, Li *et al.* (1996) found that adding limestone to

acidic soils had no effect on nonoilseed sunflower (*Helianthus annuus* L.) grain Cd concentration. Liming did not reduce the Cd status in crops in a study by Jaakola (1977) and Sparrow *et al.* (1993), and has in some cases liming has resulted in increased crop Cd concentration (Sparrow *et al.* 1993; Maier *et al.* 1997). One explanation offered for this phenomenon is that calcium ions added through lime application desorb some of the surface-bound Cd into soil solution (Maier *et al.* 1997). However, for this mechanism to have any significance, the pH-induced increase in Cd sorption with liming would need to be less than the Ca^{2+} induced desorption.

2.11.2 Total Cadmium

Total soil Cd concentrations in soil have in a number of studies been found to be of equal importance to soil pH when investigating plant Cd uptake (John *et al.* 1972; Lund *et al.* 1981; Alloway 1986). Generally, the higher the soil Cd concentration, the greater the plant Cd concentration. As a soil factor controlling Cd phytoavailability, total soil Cd concentration is not easily changed, however the rate of Cd accumulation in soils can be regulated from fertiliser or sewage sludges inputs. Regulation of maximum Cd concentrations in phosphatic fertiliser for example have been implemented in a number of countries as outlined in section 2.5.3.

2.11.3 Soil salinity

Bingham *et al.* (1986) studied the potential of chloride and sulphate salinity to affect uptake of Cd in Swiss chard (*Beta vulgaris* L.). It was found that a significant increase in the soluble Cd concentration in the soil, lead to an elevated leaf Cd concentration as a result of the application of chloride salts in combination with $Cd(NO_3)_2$, however sulphate had little effect. McLaughlin *et al.* (1994a) have recently shown that soil salinity was a major factor associated with high tuber Cd concentrations in a range of potato (*Solanum tuberosum* L.) crops irrigated with high chloride waters in South Australia (Figure 2.3). A study by Li *et al.* (1994) also demonstrated that the soil chloride concentration was an important factor related to Cd uptake in sunflower plants. The relationship between soil chloride concentration and Cd availability for plants is not fully understood. A proposed effect of salinity is due to chloro-complexation of Cd^{2+} releasing sorbed Cd into soil solution (McLaughlin and Tiller 1994). Also it could be through exchange of sorbed Cd by

the cation (Ca) associated with the chloride salt (Li *et al.* 1994). In addition, Smolders and McLaughlin (1996) and McLaughlin *et al.* (1997) have suggested that the lower charge on the Cd ion after complexation with Cl allows greater concentrations of $CdCl_n^{2-n}$ species (i.e. $CdCl^+$, $CdCl_2^0$) in soil solution which may enhance plant uptake.

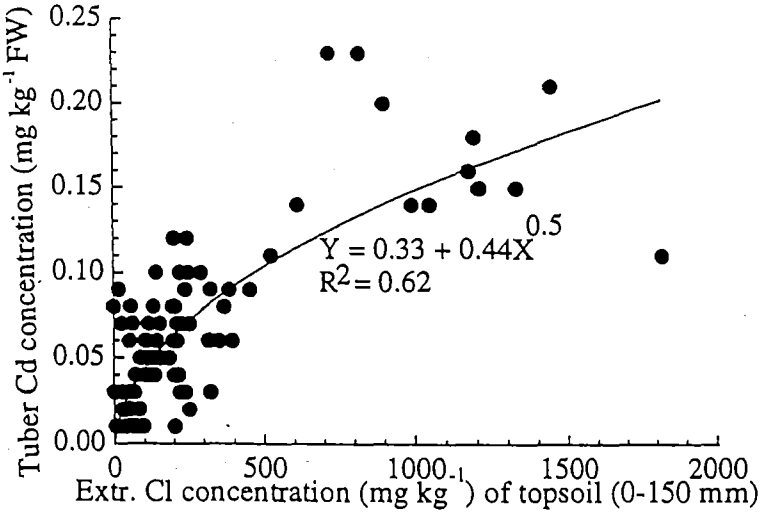

Figure 2.3 Relationship between tuber cadmium concentrations and extracatable Cl^- concentrations in soil (from McLaughlin *et al.* 1994a).

2.11.4 Micronutrients

Another important soil factor controlling plant Cd concentration is soil micronutrient status, in particular soil Zn concentration. Studies have demonstrated no effect, synergistic, and antagonistic relationships between soil Zn and plant Cd concentrations. Haghiri (1974) for example found additions of Zn to soil increased Cd concentrations of soybean (*Glycine max* L.) shoots. However a number of others studies, involving a range of crops e.g. lettuce (*Lactuca sativa* L.) (MacLean 1976), barley (*Hordeum vulgare* L.) (Singh and Steinnes 1976) found that Cd uptake was independent of the Zn treatment. In contrast, Abdel-Sabour *et al.* (1988) found application of Zn at rates of 0-50 mg kg^{-1} decreased Cd concentrations in Swiss chard and maize (*Zea mays* L.) grown in a glasshouse study. Similarly, Honman and Hirata (1978) observed decreased Cd uptake in rice (*Oryza sativa* L.) upon amelioration of Zn deficiency. McLaughlin *et al.* (1993) also report a reduction in the Cd content of potato tubers when Zn is applied to a Zn adequate soil. Oliver *et al.* (1994) showed that Cd concentrations in wheat grain can be decreased by up to 50 % by

addition of 2.5 - 5.0 kg Zn ha^{-1} to soils marginally or severely Zn deficient (Figure 2.4). Similar results were observed for flax (*Linum usitatissimum* L.) by Moraghan (1993). The effectiveness of foliar applications of Zn to decrease Cd concentrations in crops has also been investigated. Choudhary *et al.* (1994) found that Zn applied to soil decreased Cd concentration in durum wheat grain (*Triticum turgidum* L.), however foliar applications of Zn had no effect on grain Cd concentration. Oliver *et al.* (1997) recently showed that foliar application of Zn can reduce Cd concentration in wheat grain although the amount of Zn applied would have to be higher than current recommended concentrations applied to ameliorate Zn deficiency in wheat crops. It appears that Zn may play an integral role in Cd availability for a number of crops. However its success in reducing Cd uptake appears dependent on soil Zn status and method of application.

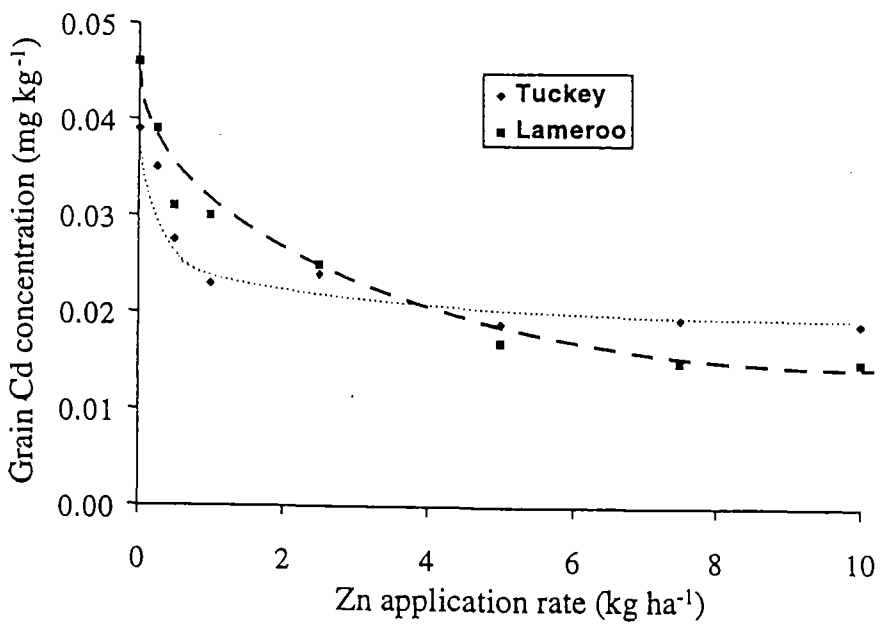

Figure 2.4 Effect of small applications of zinc on grain cadmium concentrations in wheat at two sites in South Australia (modified from Oliver *et al.* 1994).

2.11.5 Macronutrients

Fertiliser additions to soil can increase Cd concentration in the soil solution, even if the fertiliser contains no Cd, through the effect of fertiliser application on soil pH and ionic

strength of the soil solution (Andersson 1976; Naidu *et al.* 1994). A study by Williams and David (1976) showed that wheat crops accumulated more Cd when fertilised with NH_4NO_3 in conjunction with superphosphate compared to superphosphate alone. This result maybe related to ammonia based fertiliser inducing localised acidification or increased ionic strength in the soil solution thereby increasing solution Cd concentrations. Eriksson (1990) and Willaert and Verloo (1992) have also shown that acidifying N fertilisers (e.g. ammonium sulphate) increased Cd uptake compared to alkaline fertiliser (e.g. nitrate based). In addition, Mitchell *et al.* (1997), in their study confirmed that N fertilisers could increase the solubility of Cd and increase its availability to plants. However their work showed that increased ionic strength rather than pH was more important with regard to Cd phytoavailability. Grant *et al.* (1996) showed that additions of NH_4NO_3 fertiliser increased Cd concentrations in barley as well as increased crop yield, and commented that increased Cd accumulation could be a result of increased root interception and enhanced mass flow.

Although potassium has little effect on Cd availability, the associated sulphate or chloride anions are important (McLaughlin *et al.* 1996). In a recent field study, Sparrow *et al.* (1994) found that four out of six potato crops fertilised with KCl accumulated greater Cd concentrations than those fertilised with K_2SO_4 fertiliser. Similarly, Grant *et al.* (1996) showed that the application of KCl fertiliser tended to increase Cd concentrations in malting barley. They indicated that the chloride component of KCl fertiliser can form complexes with Cd which could increase the mobility of Cd in the soil system and its phytoavailability. In contrast, McLaughlin *et al.* (1995) found no effect on potato Cd concentration when KCl and K_2SO_4 fertiliser application were compared.

2.11.6 Plant species and cultivars

It has been shown that different plant species and cultivars within species accumulate Cd to different degrees if grown on the same soil (MacLean 1976; Chaney and Hornick 1978; McLaughlin *et al.* 1994b; Oliver *et al.* 1995; Hamon *et al.* 1997). In general, when grown in the same soil, Cd accumulation by different plant species has been shown to decrease in the order, leafy vegetables > root vegetables > grain crops (Bingham 1979; Page *et al.* 1987). Hamon *et al.* (1997) found large variations in the amounts of Cd taken up by different plant species. Highest concentrations of Cd were found in capeweed (*Arctotheca*

calendula L.) and lettuce, with lowest in wheat. The mechanism behind the ability of different plant species to mobilise, and hence, access different fractions of Cd in soils is still unclear. Cakmak *et al.* (1994) for example showed that some monocotyledon species growing in soil deficient in Fe and Zn, could release metal-mobilising root exudates which would enhance uptake of these metals. Thus differences in ability of plants to accumulate metals may be due to quantitative and/or qualitative differences in their root exudates which influence quantity of metals extracted from the soil (Mench and Martin 1991).

Cultivar differences for Cd uptake have been documented for a range of crops, including maize, barley, wheat, non-oilseed sunflower, soybean, lettuce, potatoes, and carrots (Boggess *et al.* 1978; Hinesly *et al.* 1978; Chang *et al.* 1982; Harrison 1986; Thomas and Harrison 1989; McLaughlin *et al.* 1994b; Li *et al.* 1995; Oliver *et al.* 1995). Chaney *et al.* (1993) examined 200 sunflower genotypes for their ability to reduce uptake and translocation of Cd to kernels. They found a significant range in genotypic variation, with a four fold range in Cd concentrations for mean kernel concentrations. Likewise, Bell *et al.* (1997) found at least a two fold variation in the Cd content among a number of peanut (*Arachis hypogaea* L.) varieties in north-eastern Australia. McLaughlin *et al.* (1994b) discovered significant differences in Cd concentration in potato tubers for a number of different cultivars (Figure 2.5). Moreover, tuber Cd concentration could be reduced at some sites by up to 50 % by appropriate choice of cultivar. More recently, Oliver *et al.* (1995) found considerable variation in grain Cd concentrations in many of the Australian wheat cultivars studied. Cieslinski *et al.* (1996) also found Cd accumulation in wheat grain was strongly affected by wheat cultivar in Canada. As a consequence of this research, plant breeding programs are trying to develop crop cultivars which tend to accumulate relatively low levels of Cd in plants. This is the case currently in North America where attempts are being made at producing cultivars of durum wheat and flax with reduced seed Cd concentrations (Li *et al.* 1995; Penner *et al.* 1995).

2.11.7 Soil temperature

There is some evidence to suggest that soil temperature can affect plant uptake of Cd. Haghiri (1974) showed that with an increase in soil temperature from 15.5°C - 32.2°C, there was an increase in Cd accumulation in soybean shoots from 5.16 to 9.47 mg kg^{-1}.

Giordana *et al.* (1979) found that the effect of soil temperature on plant Cd uptake was less clear cut. Soil heating significantly increased Cd concentrations in broccoli and potato, but there was no statistically significant increase in other vegetables crops grown. Chang *et al.* (1987) investigating long term sludge application of Cd and Zn accumulation in Swiss chard and radish, found that environmental conditions including soil temperature influenced Cd accumulation in plant tissue. Hooda and Alloway (1993) showed that Cd uptake by ryegrass (*Lolium perenne* L.) from soils amended by Cd salts and sludge application was significantly higher in pots in the warm (25°C) environment than those from the cool (15°C) environment.

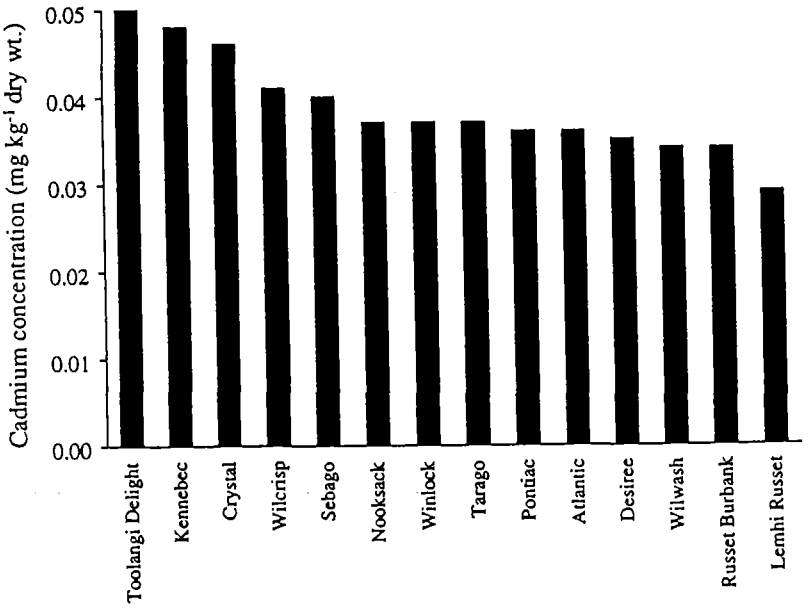

Figure 2.5 Mean cadmium concentrations for major potato cultivars averaged over a range of sites throughout Australia: n=4 to 8 for any single cultivar (from McLaughlin *et al.* 1994b).

2.11.8 Soil redox conditions

Oxidation-reduction potential of soil also can influence Cd uptake from soils by plants. Bingham *et al.* (1976) have shown that the concentration of Cd in rice grown under reducing conditions (flooded) is less that that of rice grown under oxidising conditions. Similar observations have been made by Reddy and Patrick (1977) who found that total Cd

uptake and shoot uptake by rice plants grown in soil suspensions was greater with increased suspension redox potential and a decrease in pH.

2.11.9 Other factors

There is some evidence to indicate that Cd accumulation in some crops can be higher when grown in rotation with certain restorative crops e.g. lupins. Oliver *et al.* (1993) found that Cd concentrations in wheat grain were highest when grown in rotation with lupins, and was lowest when grown after either continuous wheat or in rotation with barley (Figure 2.6). Although not fully explained, the result may be partially related to decreases in soil pH commonly observed with legume growth or decomposition products of the lupin stubble. A similar crop rotation effect on wheat Cd has been found for crops following flax (Bailey *et al.* 1995).

Tillage management may impact on soil pH and nutrient stratification in the soil, which may influence availability of Cd for plant uptake. Placement (Grant and Bailey 1997) and source (McLaughlin *et al.* 1995) of fertilisers may also influence crop Cd content.

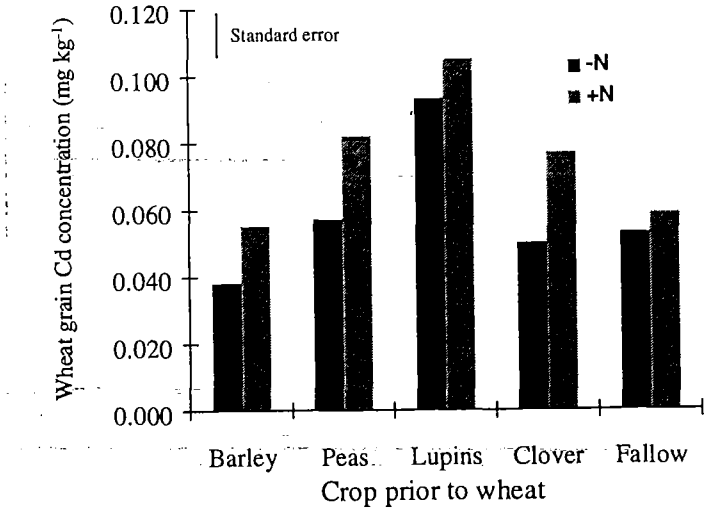

Figure 2.6 Effect of crop rotations on cadmium concentrations in wheat at Tarlee, South Australia (from Oliver *et al.* 1993).

2.12 Determination of plant available Cd in soils

The usefulness of a soil extractant to predict the plant available fraction of soil Cd depends on its ability to simulate soil solution conditions during the extraction e.g. pH, ionic strength. The majority of studies examining the relationship between plant uptake of Cd from soils and the Cd in soil extracts have been carried out with Cd added to soils, either as soluble inorganic salts (Symeonides and McRae 1977; Brams and Anthony 1988; Eriksson 1989; Xue and Harrison 1991; Smilde *et al.* 1992; Han and Lee 1996) or using soil contaminated by sewage sludge application (Alloway *et al.* 1990; Jackson and Alloway 1991; Jing and Logan 1992). Additionally, studies developing soil tests for plant available Cd have often been undertaken at very high Cd concentrations (e.g. > 100 mg kg^{-1}) (Symeonides and McRae 1977; Lee and Zheng 1993).

There are numerous laboratory methods that have been proposed and evaluated to measure Cd phytoavailability in soils (Table 2.9). These soil extractants can be broadly grouped in the following categories:

1. Weak salts (e.g. $CaCl_2$, NH_4Cl);
2. Chelating agents (e.g. EDTA, DTPA);
3. Weak acids (CH_3COOH);
4. Dilute solutions of strong acids (e.g. HCl, HNO_3).

The efficiency and predictability of a given extractant can be strongly influenced by soil and plant factors, and as a consequence there is no universal extractant for Cd. Symeonides and McRae (1977) compared seven extractants, and found the highest significant relationship between Cd concentration in radish and unbuffered 1 M NH_4NO_3 solution. These authors also found significant correlations with 1 M NH_4OAc and 5 % CH_3COOH, however stressed the greater efficiency of 1 M NH_4NO_3 because the natural pH of the soil is maintained, and it is pH which has a marked effect on Cd availability to plants. Similar conclusions were drawn by He and Singh (1994) and Guttormsen *et al.* (1995) who showed that 1 M NH_4NO_3 was sensitive to soil pH. However, Krishnamurti *et al.* (1995b) showed data that in comparison with 6 other existing soil test methods for bioavailable Cd, extraction of the soil with unbuffered 1 M NH_4Cl provided the best measure of Cd uptake

for durum wheat. Numerous other workers however have favoured neutral 1 M NH_4OAc as a measure of Cd phytoavailability e.g. John *et al.* (1972) radish and lettuce; Haghiri (1974) oat (*Avena sativa* L.); Andersson and Nilsson (1974) fodder rape and Soon and Bates (1982) maize (*Zea mays* L). Andrewes *et al.* (1996) comparing 6 different extractants to predict plant available Cd on soils that had accumulated Cd under "normal" New Zealand agricultural practices found that 0.01 M $CaCl_2$ to be the best indicator of plant available Cd. Andrewes *et al.* (1996) argued that $CaCl_2$ is sensitive to the soil factors which are known to contribute to plant uptake of Cd e.g. pH, organic matter and P fertiliser application. Similarly, Whitten and Ritchie (1991) found 0.01 M $CaCl_2$ an excellent predictor of the Cd status in clover (*Trifolium subterraneum* L.) for Australian soils. These authors state that $CaCl_2$ extracts at the ionic strength of the soil solution and is more appropriate than acidic or buffered extractants because the pH of $CaCl_2$ extracts is similar to that in the soil. Chelating agents such as EDTA (ethylene diamine tetraacetic acid) and DTPA (diethylene triamine pentaacetic acid) have also been used to predict of Cd phytoavailability. Jackson and Alloway (1991) for example showed EDTA could predict Cd concentration in lettuce and cabbage, although stronger relationships were found using $CaCl_2$.

Weak acids have also been evaluated. Haq *et al.* (1980) tested nine soil extractants and found that 0.5 M CH_3COOH was the best extractant for predicting plant available Cd when soil pH was included in the regression equation. Extractable Cd and soil pH accounted for 81% of the variability of Swiss chard Cd concentration.

An alternative approach for estimating Cd phytoavailability is using chelating resin membranes, which introduces a strong infinite sink into the soil for Cd to bind. This method is less destructive than chemical extractants and its reaction is thought to more resemble the way plants extract elements from the soil (Lee and Zheng 1993).

Table 2.9 Chemical reagents used for cadmium extraction by different workers

Extractant	Soil/Soln. ratio	Time of extract (h)	Reference
0.01 M $CaCl_2$	1:5	16 h	Whitten and Ritchie (1991)
0.1 M $CaCl_2$	1:2.5	not given	(Smilde *et al.* 1992)
0.05 $CaCl_2$	1:6	16 h	(Jackson and Alloway 1991)
1 M NH_4NO_3	1:10	1 h	Symeonides and McRae (1977)
1 M NH_4Cl	1:6	16 h	Krishnamurti *et al.* (1995b)
0.005 M DTPA			
+ 0.1 M TEA	1:2	2 h	Lindsay and Norvell (1978)
+ 0.01 M $CaCl_2$ (pH 7.3)			
1 M NH_4OAc	1:10	0.5	John *et al.* (1972)
0.05 M EDTA	1:6	1 h	(Jackson and Alloway 1991)
0.05 M $Ca(NO_3)_2$	1:10	16 h	(Jing and Logan 1992)
Chelex Resin Membrane			(Lee and Zheng 1993).
1 N HCl	1:2	1 h	Lagerwerff (1971)
0.04 M AAAc-EDTA	1:10	1 h	Lakanen and Ervio (1971)
0.5 N CH_3COOH (pH 7.0)	1:10	0.5 h	Haq *et al.* (1980)
AB-DTPA (pH 7.6)	1:2	0.25	Soltanpour and Schwab (1977)

2.13 Project objectives

1. To study sorption and desorption of native and added Cd at low Cd concentrations for a range of New Zealand soils, and relate this to physical and chemical soil properties;
2. Examine the effect of soil pH and contact time on sorption and desorption of native and added Cd;
3. Evaluate the suitability of a number of commonly used soil extractants to predict the plant uptake of Cd for a number of plant species;
4. Investigate plant Cd concentration for a range of plant species;
5. Evaluate the effect of soil pH on plant Cd concentration;
6. Investigate the effects of long-term phosphatic fertiliser applications on amounts and forms of cadmium in a soil under irrigated pasture in New Zealand.

Chapter 3

Materials and Methods

Twenty-one New Zealand topsoils samples from both the North and South Islands were selected for study. The soils were selected to represent a wide range of soil properties (e.g. organic carbon, soil pH, free oxides, soil texture and total soil Cd). The New Zealand classification of the soils used in this study is shown in Table 3.1.

Table 3.1 Classification of experimental soils

	Soil series	NZ Soil Classification	NZ Genetic Classification
1	Ohura silt loam	Brown Soil	Yellow brown earth
2	Te Kuiti silt loam 1	Orthic Allophanic Soil	Yellow brown loam
3	Whakatane silt loam	Orthic Allophanic Soil	Yellow brown loam
4	Taupo sandy loam	Orthic pumice Soil	Yellow brown pumice
5	Temuka peaty silt loam	Orthic Gley Soil	Gley soil
6	Waimakariri sandy loam	Recent soil	Recent soil
7	Summit silt loam	Orthic Brown soil	Upland Yellow brown earth
8	Waiareka clay loam 1	Vertic Melanic Soil	Brown granular loam
9	Tai Tapu silt loam	Recent soil	Gley recent soil
10	Temuka clay loam 1	Orthic Gley soil	Gley soil
11	Patumahoe clay loam	Orthic Granular Soil	Northern brown granular loam
12	Te Kowhai silt loam	Orthic Gley Soil	Gley soil
13	Te Kowhai humic silt loam	Orthic Gley Soil	Gley soil
14	Te Rapa peaty silt loam	Orthic Podzol	Podzol
15	Motumaoho silty peat	Humic Organic Soil	Organic soil
16	Kaipaki peat	Mesic Organic Soil	Organic soil
17	Waiotira silt loam	Yellow Ultic Soil	Nothern Yellow brown earth
18	Te Kuiti silt loam 2	Orthic Allophanic Soil	Yellow brown loam
19	Waiareka clay loam 2	Vertic Melanic Soil	Brown granular loam
20	Takahe silt loam	Fragic pallic Soil	Southern yellow-grey earth
21	Temuka clay loam 2	Orthic Gley Soil	Gley soil

1. Soils 1 - 11 were used in two pot trial experiments (chapters 6 and 7).
2. Soils 12 - 17 were samples from a liming trial, and as a consequence there were three samples with varying pH per soil (c. 18 samples total), these samples were used in chapter 4 along with soils 18 - 21.
3. Soils 1 -11 were combined with samples 12 -17 with varying pH, for analysis in chapter 5, where the soils are numbered 1 - 29.

3.1 Soil Characterisation

All soils were dried at 20 °C in a drying cabinet and ground to pass through a 2 mm stainless steel sieve. Soils were stored in polyethylene containers or bags at room temperature prior to analysis.

3.1.1 Soil texture

Soil particle size distribution was determined by the International Pipette method (Day 1965).

3.1.2 pH_{water}

Air dried soil (10 g) was stirred with 25 mL of deionised water, left overnight to equilibrate and pH was read on a pH meter (Blakemore *et al.* 1987).

3.1.3 Total carbon

Organic carbon was determined by a LECO 2000 CNS analyser at 1300 °C.

3.1.4 Olsen P

One gram of soil was extracted with 20 mL of 0.5 M $NaHCO_3$ (pH 8.5, adjusted with NaOH) on an end-over-end shaker for 30 minutes. Samples were centrifuged at 10 000 rpm for 10 minutes and filtered through Whatman No. 42 filter paper. The phosphate concentration in the extract was then determined using molybdenum blue (Murphy and Riley 1962) colour reaction as described by Blakemore *et al.* (1987) on a Shimadzu Double-beam spectrophotometer UV-140-02 at a wavelength of 880 nm.

3.1.5 Total Phosphorus

Total phosphorus was determined by NaOH fusion after the method of Smith and Bain (1982) and as adapted by Blakemore *et al.* (1987).

3.1.6 Cation exchange capacity

The cation exchange of soils was determined by ammonium acetate leaching at pH 7.0 (Blakemore *et al.* 1987).

3.1.7 Amorphous iron and aluminium oxides

One gram of soil was equilibrated with 50 mL of acid oxalate reagent (0.2 M ammonium oxalate, 0.2 M oxalic acid, pH 3) in the dark on an end-over-end shaker for 4 hours (McKeaque and Day 1966). The contents were centrifuged at 10 000 rpm and filtered through a No. 42 Whatman filter paper and Fe and Al were determined in the extract using a Shimadzu flame atomic absorption spectrophotometer.

3.1.8 Crystalline iron and aluminium oxides

One gram of soil was equilibrated with 50 mL of acid oxalate ascorbic acid reagent (0.2M ammonium oxalate; 0.2 M oxalic acid; 0.1 M ascorbic acid, pH 3). Extraction was carried out in a boiling water bath for 30 minutes with occasional stirring (Shuman 1982). The contents were centrifuged at 10 000 rpm and filtered through a No. 42 Whatman filter paper and Fe and Al was determined as for amorphous Fe and Al, with results corrected for amorphous Fe and Al.

3.1.9 Manganese oxides

One gram of finely ground soil was equilibrated with 20 mL of 0.1 M hydroxyl-amine hydrochloride (pH 2) for 30 minutes on an end-over-end shaker (Chao 1972). The contents were centrifuged at 10 000 rpm and filtered through a No. 42 Whatman filter paper. Manganese was determined in the filtrate using a flame atomic absorption spectrophotometer.

3.1.10 Cadmium analysis

3.1.10.1 Total soil cadmium

Total Cd in soils was determined by the USEPA SW 846-Method 3051 which is a microwave-based digestion. One half gram of soil is digested in 10 mL 69% Aristar grade nitric acid, and the digests made up to 25 mL volume with deionised water. Cadmium was analysed by graphite furnace atomic absorption spectrophotometry (GFAAS) using the heating parameters in Table 3.2, with a deuterium background correction and 0.1% H_3PO_4 acid was used as a modifier.

Total Cd determined by the nitric acid microwave digestion method is considered a 'pseudo-total' because this method does not solubilise silicate minerals as may be expected in a 'true' total metal concentration using for example HF acid. However, it is assumed that applied Cd will not be held within the crystal lattice of primary minerals, with Cd within these structures geogenic rather than anthropogenic in origin (Clayton and Tiller 1979). Moreover, Krishnamurti *et al.* (1994) has compared a nitric microwave digestion technique with a more conventional HF-$HClO_4$ digestion, and found the nitric microwave method solubilised >95% of the total Cd. Boekhold and Van der Zee (1992), Nicholson *et al.* (1995), Soon and Abboud (1993) consider a nitric acid digestion would give a good estimate of potentially available metals.

Table 3.2 Graphite furnace heating parameters for total and plant Cd concentrations

Step	Final Temp (°C)	Ramp Time (s)	Hold Time (s)	Gas Type	Read	Signal Graphics
Step 1	100	20.0	5.0	Inert	Off	Off
Step 2	250	10.0	2.0	Inert	Off	Off
Step 3	400	10.0	2.0	Inert	Off	Off
Step 4	400	1.1	2.0	None	Off	Off
Step 5	1700	1.1	1.0	None	On	On
Step 6	2500	1.0	0.0	Inert	Off	Off

3.1.10.2 Plant cadmium

Ground plant material (0.5g) was digested in 10 mL 69% Aristar grade nitric acid and heated on a digestion block up to 140 °C over a period of 7 h. The digest was then made up to 20 mL with deionised water and filtered through a Whatman No. 42 paper filter paper prior to analysis. Cadmium was analysed by as for total Cd (3.1.10.1).

3.1.10.3 Solvent extraction of cadmium

Cadmium in extracts which contain high salt concentrations was subjected to complexing with organic reagents. Cadmium in filtrate extracts was complexed with ammonium pyrrolidine dithiocarbamate (APDC) and extracted into 4-methyl isobutyl ketone (MIBK) according to the method of Dudas (1974). A 5 mL aliquot of extract supernatant was sampled and 1 mL of freshly made 1 % APDC added, and the sample shaken for 15 seconds and then left to stand for 5 minutes. 4 mL of MIBK was then added and the sample again shaken for 1 min and left to stand for 20 minutes to allow the two layers to separate. 10 µL of the organic phase (top layer) was injected into the furnace. Standards were made up in the extracting solution before complexing with APDC and extracting into MIBK. Cadmium was analysed by (GFAAS) with a deuterium background correction. A slightly different heating program was used (Table 3.3), which involved a longer ramp time for steps 1 and 2.

Table 3.3 Graphite furnace heating parameters for extractable metal concentrations

Step	Final Temp (°C)	Ramp Time (s)	Hold Time (s)	Gas Type	Read	Signal Graphics
Step 1	100	50.0	5.0	Inert	Off	Off
Step 2	250	20.0	2.0	Inert	Off	Off
Step 3	400	10.0	2.0	Inert	Off	Off
Step 4	400	1.1	2.0	None	Off	Off
Step 5	1700	1.1	1.0	None	On	On
Step 6	2500	1.0	0.0	Inert	Off	Off

Chapter 4

*Sorption and desorption of cadmium from some New Zealand soils: effect of pH and contact time

4.1 Introduction

Cadmium (Cd) is considered an important environmental soil pollutant, as it is a potentially biotoxic heavy metal that is readily absorbed by plants and has potential to enter the human food chain (Chang *et al.* 1983). Cadmium can enter an agricultural system through a number of sources. These include the land disposal of sewage sludge, accumulation in soil from various industrial pollution sources or from application of phosphate fertiliser in which Cd is an impurity (Bramley 1990; Roberts *et al.* 1994). The likely phytoavailability, and hence potential toxicity of Cd in soils, is probably controlled, like other trace metals, by sorption/desorption phenomena at soil colloid surfaces (Swift and McLaren 1991). Sorption is important in soils because the persistence (Selim 1992) and transport (Boekhold and Van der Zee 1991) of Cd is governed to a large extent by sorption onto soil colloidal components. The desorption of Cd from soils is also considered an important process (Christensen 1984b). It is important to determine whether sorbed Cd is readily released from soil surfaces, and how release is affected by soil characteristics such as pH. However, the majority of work to date (e.g. Garcia-Miragaya and Page 1978; Garcia-Miragaya 1980; Kim and Fergusson 1992) has focused on describing the Cd sorption processes rather than Cd desorption. Swift and McLaren (1991) indicated that desorption is as important as sorption, in that it controls the amounts and rate of release of ions into solution and hence their phytoavailability. Also, most of the existing literature on Cd sorption involves concentrations which are too high to be relevant to the New Zealand agricultural situation (e.g. Levi-Minzi *et al.* 1976; Navrot *et al.* 1978; O'Connor *et al.* 1984) where total Cd concentrations range between 0.04 - 1.53 μg Cd g^{-1} for fertilised pasture soils (Roberts *et al.* 1994). This chapter describes experimental work that has been undertaken to investigate sorption and desorption processes in several New Zealand soils with different physical and chemical properties.

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Cadmium concentrations used were those in the range encountered in native soils or those affected by phosphorus fertiliser inputs in New Zealand. The effect of soil pH on both sorption and desorption of Cd is investigated, together with effect of contact time between soil and added Cd on subsequent Cd desorption.

4.2 Material and methods

4.2.1 Soils

4.2.1.1 Effect of pH on Cd sorption/desorption

Soils used for this study were samples of topsoil (0 - 75 mm) taken from a series of liming trials, and as a consequence the soil pH values are those as modified by lime application in the field. The soils sampled included 2 Gley Soils, 2 Organic Soils, a Podzol and an Ultic Soil (Hewitt 1993) and had textures ranging from silt loams through to a silty clay (Table 4.1). Samples were taken approximately 5 years after the initial lime applications and the pHs represent values being appropriate to most agricultural topsoils in New Zealand, i.e. 5.0 - 6.0 (Table 4.1). The use of such soil samples appears to be unique in this type of work where generally soil pH has been altered in the laboratory by addition of an acid or a base (e.g. Garcia-Miragaya and Page 1978; Singh 1979; Pardo and Guadalix 1995).

4.2.1.2 Effect of contact period on Cd desorption

The 4 soils selected for this study were shown in preliminary experiments to differ in their ability to sorb and desorb added Cd. The soils included an Allophanic Soil (Te Kuiti), a Melanic Soil (Waiareka), a Pallic Soil (Takahe) and a Gley Soil (Temuka) and were soils with a diverse range of chemical and physical properties (Table 4.2).

4.2.3 Soil preparation and analysis

All soil samples were air-dried and ground to pass through a 2 mm stainless steel sieve prior to laboratory analysis. Soil pH was measured in a water suspension using a soil:solution ratio of 1:2.5. Organic carbon content in the soils was determined by LECO CNS 2000 analyser. Total Cd was determined by a nitric acid microwave digestion method (USEPA SW 846-3051). Cation exchange capacity (CEC) was determined by ammonium acetate leaching at pH 7.0 (Blakemore *et al.* 1987). Amorphous iron (Fe) and aluminium (Al) oxides were determined by ammonium oxalate extraction (Blakemore *et*

*al.*1987). Crystalline Fe and Al oxides were determined by the oxalate/ascorbic acid extraction method of Shuman (1982), correcting the results for amorphous Fe and Al. Manganese oxide content was determined by extraction with 0.1 M hydroxyl-amine hydrochloride (Shuman 1982), bioavailable P (Olsen P) was determined by bicarbonate extraction (Blakemore *et al.* 1987), and soil texture was determined by the pipette method (Day 1965).

4.2.4 Cd sorption

Cadmium sorption was determined using a batch equilibrium technique. Cadmium was added as $Cd(NO_3)_2$ to 0.5 g soil in 20 mL of a background electrolyte of 0.01 M $Ca(NO_3)_2$. Calcium nitrate was used as the supporting electrolyte to eliminate non-specific sorption of Cd, since low affinity sorption sites would be saturated by calcium ions. Initial Cd concentrations ranged between 0.01 - 0.05 mg L^{-1}. Preliminary experiments to determine time of equilibration showed that after 24 h there was no significant change in the amount of Cd sorbed by the soil (refer section 4.3.2.1). Thus soil suspensions were shaken for 24 h, on a reciprocating shaker at 20 °C, after which the samples were centrifuged at 10 000 rpm (RCF 9,440 *g*) for 10 minutes. The pH of the supernatant was then measured prior to being filtered through a Whatman No. 42 filter paper and Cd determined in the supernatant by graphite furnace atomic absorption spectrophotometry (GFAAS) using a GBC furnace, with deuterium background correction and using a 0.1% H_3PO_4 modifier. The limit of detection (LOD) was 0.5 µg Cd L^{-1} solution (0.02 µg Cd g^{-1} soil).

4.2.5 Desorption of native Cd

Desorption of Cd from soils was determined by repeated equilibration of soil samples (5.0g) with 30 mL of Cd-free 0.01 M $Ca(NO_3)_2$. In order to obtain the required sensitivity for Cd analysis of the equilibrium solutions, a much lower soil:solution ratio was necessary compared to studies with added Cd. Equilibrations were carried out for 2 h at 20 °C. This desorption period was selected as a result of a preliminary study which showed little change in the amount of Cd desorbed from the soil after a 2 h equilibration (refer section 4.3.2.2). Following equilibration, samples were centrifuged and the supernatant was decanted, filtered and Cd measured as described above. The soil residue was resuspended in 30 mL of fresh, Cd-free 0.01 M $Ca(NO_3)_2$ and the procedure repeated 5 times. By this

Table 4.1 Properties of the soils used for the pH sorption/desorption studies

Soil	New Zealand [A] Classification	pH	Sand	Silt	Clay	Org. C	Olsen P	Mn	Fe		Al		CEC	Total Cd
									Crystal	Amorp	Crystal	Amorp		
			(%)				($\mu g\ P\ g^{-1}$)	($\mu g\ g^{-1}$)	(%)				($cmol_c\ kg^{-1}$)	($\mu g\ Cd\ g^{-1}$)
Te Kowhai silt loam	Orthic Gley Soil	5.1 5.3 6.1	29.5	32.5	37.9	5.2 4.8 5.1	18	54.92	0.65	0.60	0.06	0.77	9.7	0.36 0.30 0.30
Te Kowhai humic silt loam	Orthic Gley Soil	5.1 5.4 6.2	18.9	45.3	35.8	13.2 13.4 12.7	13	38.99	0.22	0.16	0.13	1.08	19.0	0.41 0.43 0.41
Te Rapa peaty silt loam	Orthic Podzol	4.9 5.3 5.9	21.3	60.4	18.3	17.3 17.1 17.7	20	28.06	0.17	0.39	0.14	1.41	19.0	0.63 0.62 0.58
Motumaoho silty peat	Humic Organic Soil	5.0 5.3 5.9	27.1	57.0	15.9	29.7 27.8 28.6	37	40.24	0.13	0.19	0.09	0.75	33.1	0.97 0.94 0.91
Kaipaki peat	Mesic Organic Soil	4.9 5.1 5.8	23.1	51.6	25.3	34.2 34.3 33.1	29	12.52	0.10	0.17	0.12	0.73	30.3	1.13 0.99 0.96
Waiotira silt loam	Yellow Ultic Soil	5.1 5.7 6.0	15.3	32.4	52.4	11.4 9.2 10.4	27	65.82	0.57	0.65	0.21	0.34	23.5	0.32 0.37 0.32

[A] Hewitt (1993)

Table 4.2 Properties of the soils used for the contact period study

Soil	New Zealand [A] Classification	pH	Sand	Silt	Clay	Org. C	Olsen P	Mn	Fe		Al		CEC	Total Cd
			(%)				($\mu g\ P\ g^{-1}$)	($\mu g\ g^{-1}$)	Crystal (%)	Amorp (%)	Crystal (%)	Amorp (%)	($cmol_c kg^{-1}$)	($\mu g\ Cd g^{-1}$)
Te Kuiti silt loam	Orthic Allophanic Soil	5.2	30.6	51.4	19.0	11.5	4	39.58	0.83	0.56	0.26	3.33	23	0.48
Waiareka clay loam	Vertic Melanic Soil	6.5	23.2	38.0	38.8	6.9	62	434.69	0.89	0.76	0.42	0.43	31	0.35
Takahe silt loam	Fragic pallic Soil	5.4	17.9	61.1	21.1	2.6	13	47.69	0.66	0.29	0.29	0.11	10	0.10
Temuka clay loam	Orthic Gley Soil	5.6	9.3	49.1	41.7	5.9	14	7.19	0.56	0.36	0.26	0.12	27	0.12

[A] Hewitt (1993)

stage, very little Cd could be detected in the equilibrium solutions, particularly for the high pH samples. The LOD for each equilibration was 3 μg Cd kg^{-1} soil.

4.2.6 Desorption of added Cd

The centrifuged residues from the highest sorption concentration i.e. 2 μg Cd g^{-1}, were weighed to determine entrained Cd, resuspended in a fresh Cd-free 20 mL volume of 0.01 M $Ca(NO_3)_2$ and equilibrated for 2 h at 20 °C. Following equilibration, samples were centrifuged and the supernatant decanted, filtered and Cd measured as described above. The soil residue was reweighed and resuspended in a fresh 20 mL volume of 0.01 M $Ca(NO_3)_2$, and the procedure repeated 10 times. A larger number of equilibrations was used compared to native Cd desorption because Cd could still be detected in the equilibrium solutions after 5 desorptions. However, for most samples after 10 desorptions, particularly at high pH, little further Cd could be desorbed. The pH of the supernatant was determined at the end of each 2 h desorption period and was found to remain constant throughout the 10 successive desorption events, with the values 0.3-0.4 pH units lower than those measured in soil:water suspensions for each soil (Table 4.1). The LOD for each desorption was the same as for Cd sorption.

4.2.7 Contact period incubation

Three 200 g samples of each soil were treated with 20 mL of cadmium nitrate solution supplying 2 μg Cd g^{-1} air-dry soil. The soils were transferred to 600 mL polypropylene containers with perforated lids, wetted up to field capacity and placed in an incubator at 25 °C. At regular intervals, incubated samples were made up to field capacity by weight with deionised-distilled water. Sub-sampling for analysis was carried out immediately after this moisture addition and samples were subjected to desorption in the same manner as described above. Subsampling occurred at 5, 30 and 70 day intervals and soil pH was determined at the same intervals and found to remain constant.

All sorption and desorption work was carried out in duplicate and all data presented represent means values of the duplicate determinations. Variation between duplicates was less than 2 %.

4.3 Results and Discussion

4.3.1 Soils

Table 4.1 shows that total soil Cd concentrations ranged from 0.30 to 1.13 μg Cd g^{-1} soil and that there were no substantial differences in total Cd between different pH treatments within a particular soil. Highest total Cd concentrations were found in the Organic Soils, which were at the mid to high end of the range for Organic Soils as reported by the survey work of Roberts *et al.* (1994). The lowest total Cd concentration was in the Te Kowhai silt loam, which again is in the range determined for Gley Soils (Roberts *et al.* 1994). Soil organic carbon values ranged from medium to very high (Blakemore *et al.* 1987) and soil pH had no effect on soil carbon within a particular soil.

4.3.2 Preliminary analysis

4.3.2.1 Sorption kinetics

There have been a number of equilibration periods used in Cd sorption studies. These include 1 h (Christensen 1984a), 3 h (Hooda and Alloway 1994), 4 h (Narwal and Singh 1995); 18 h (Buchter *et al.* 1989), 24 h (Naidu *et al.* 1994; Petruzzelli *et al.* 1985), 48 h (Kim and Ferguson 1992) 7 days (Tiller *et al.* 1984a). Christensen (1984a) reported that greater than 95% of Cd sorption occurred within 10 min, and that equilibrium was achieved within 1 h. Similarly, Pardo (1997) found that after 20 min there was practically no change in the amount of Cd retained by soils, however a 1 h equilibrium time was decided upon. Kim and Fergusson (1992) showed that over 99% of Cd sorbed by a clay was sorbed in the first 48 h. Kookana *et al.* (1994) found 95% of the sorption by a spodosol was completed within 30 min, and further change occurred between 3 - 312 h. For an Oxisol however, sorption proceeded at a much slower rate, suggesting a diffusion controlled process. In the present study, sorption appeared to reach a stationary state after 24 h for three soils examined in a preliminary study (Table 4.3).

Table 4.3 The effect of shaking time on the percentage of Cd sorbed on three soils

Soil	Equilibrium time					
	0.25 h	0.5 h	1 h	5 h	24 h	48 h
8	81.54	87.19	90.84	94.19	97.88	95.46
6	22.85	22.45	30.78	35.30	36.69	34.05
2	5.00	9.20	16.20	30.14	28.78	30.60

4.3.2.2 Desorption kinetics

The concentrations of added Cd desorbed after different shaking periods with 0.01 M $Ca(NO_3)_2$ from two soils (6, 8) are presented in Table 4.4. The results indicated that a quasi-stationary state was achieved within 30 mins of shaking in both soils. Kookana *et al.* (1997) showed that the amount of Cd desorbed also using 0.01 M $Ca(NO_3)_2$ did not significantly change after a 2 h shaking period. To ensure a sufficient period for the system to reach equilibrium, a 2 h shaking time was adopted for all the desorption experiments.

Table 4.4 The effect of shaking time on 0.01 M $Ca(NO_3)_2$ extractable Cd

Soil	Cd desorbed (μg g^{-1} soil) after				
	0.5 h	1 h	2 h	4 h	24 h
6	0.402	0.416	0.423	0.418	0.427
8	0.116	0.110	0.107	0.099	0.109

4.3.3 Native Cd desorption

For the purposes of this study, native soil Cd is considered as Cd already present in the soil, having been derived from the soil parent material and Cd which has accumulated in the soil from the application of phosphatic fertiliser. Native Cd desorption data is plotted as cumulative amounts of Cd desorbed (μg Cd kg^{-1}) with 5 successive equilibrations in 0.01 M $Ca(NO_3)_2$. Typical examples for 2 soils are shown in Fig. 4.1, (data for other soils are shown in Appendix 4.1). The plots show that compared to high pH values, at low soil pH more native Cd seems to be desorbed, while as soil pH increases, Cd desorption levels out and at the highest pHs very little Cd is released from the soil. Increasing soil pH for all 6 soil samples resulted in a substantial reduction in the amount of native Cd desorbed (Table 4.5). For all 6 soils, the cumulative amounts of Cd desorbed by 5 desorption equilibrations represented only relatively small proportions (0 to 22%) of the total soil Cd concentrations (Table 4.5). The largest cumulative desorption occurred in the Te Kowhai silt loam with least in the Kaipaki peat.

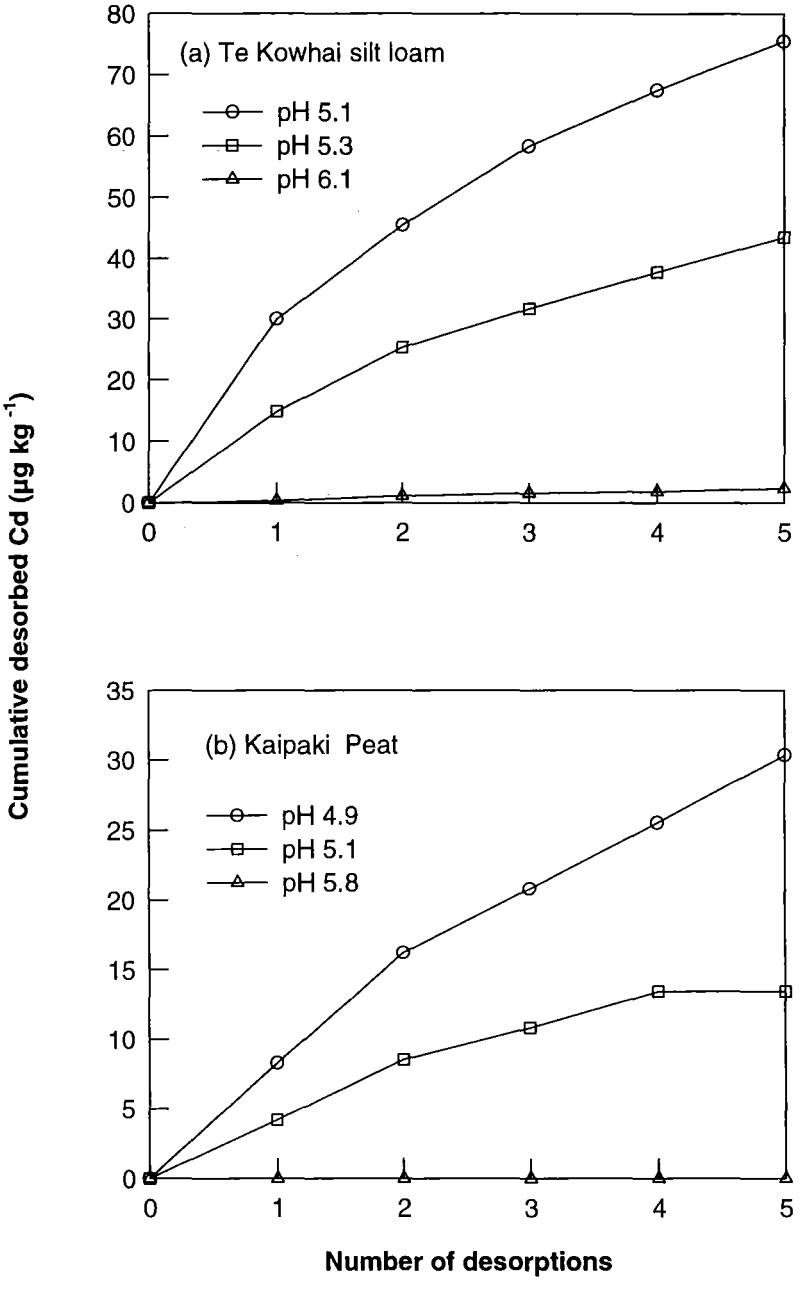


Fig. 4.1 Effect of pH on cumulative desorption of native Cd from (a) Te Kowhai silt loam and (b) Kaipaki peat.

Table 4.5 Effect of pH on cumulative desorption of native cadmium

Soil	pH	Native Cd desorbed	
		μg Cd kg^{-1} soil	(% of total Cd)
Te Kowhai silt loam	5.1	78.56	22.1
	5.3	43.41	14.7
	6.1	2.33	7.7
Te Kowhai humic silt loam	5.1	26.38	6.4
	5.4	17.65	4.1
	6.2	0.00	0.0
Te Rapa peaty silt loam	4.9	61.26	9.7
	5.3	38.89	6.3
	5.9	2.70	0.5
Motumaoho silty peat	5.0	26.15	2.7
	5.3	17.74	1.9
	5.9	0.00	0.0
Kaipaki peat	4.9	30.33	2.7
	5.1	13.43	1.4
	5.8	0.00	0.0
Waiotira silt loam	5.1	37.35	11.6
	5.7	32.12	8.8
	6.0	1.50	4.7

4.3.4 Cd sorption

Typical examples of Cd sorption isotherm plots constructed for two of the soils studied, at pH values ranging from pH 4.9 to pH 6.2 are shown in Fig. 4.2, (data for other soils are shown in Appendix 4.2). Sorption of added Cd (2 μg Cd g^{-1}) ranged between 38% and 96% (Table 4.6). The sorption isotherms in all cases were linear, a feature also noted by a number of previous workers investigating Cd sorption at low concentrations (Garcia-Miragaya and Page 1978; Petruzzelli *et al.* 1985; Boekhold *et al.* 1993). The linearity is indicative of a constant partition coefficient between the soil and the solute, and this is often the case at low solution concentrations. Sposito (1984) describes this type of adsorption isotherm as a C-curve isotherm, where the initial slope remains independent of adsorptive concentration. As expected at such low solution concentrations, sorption maxima were not reached. Tiller *et al.* (1979) remarked that sorption maxima generally have little relevance to problems of soil contamination.

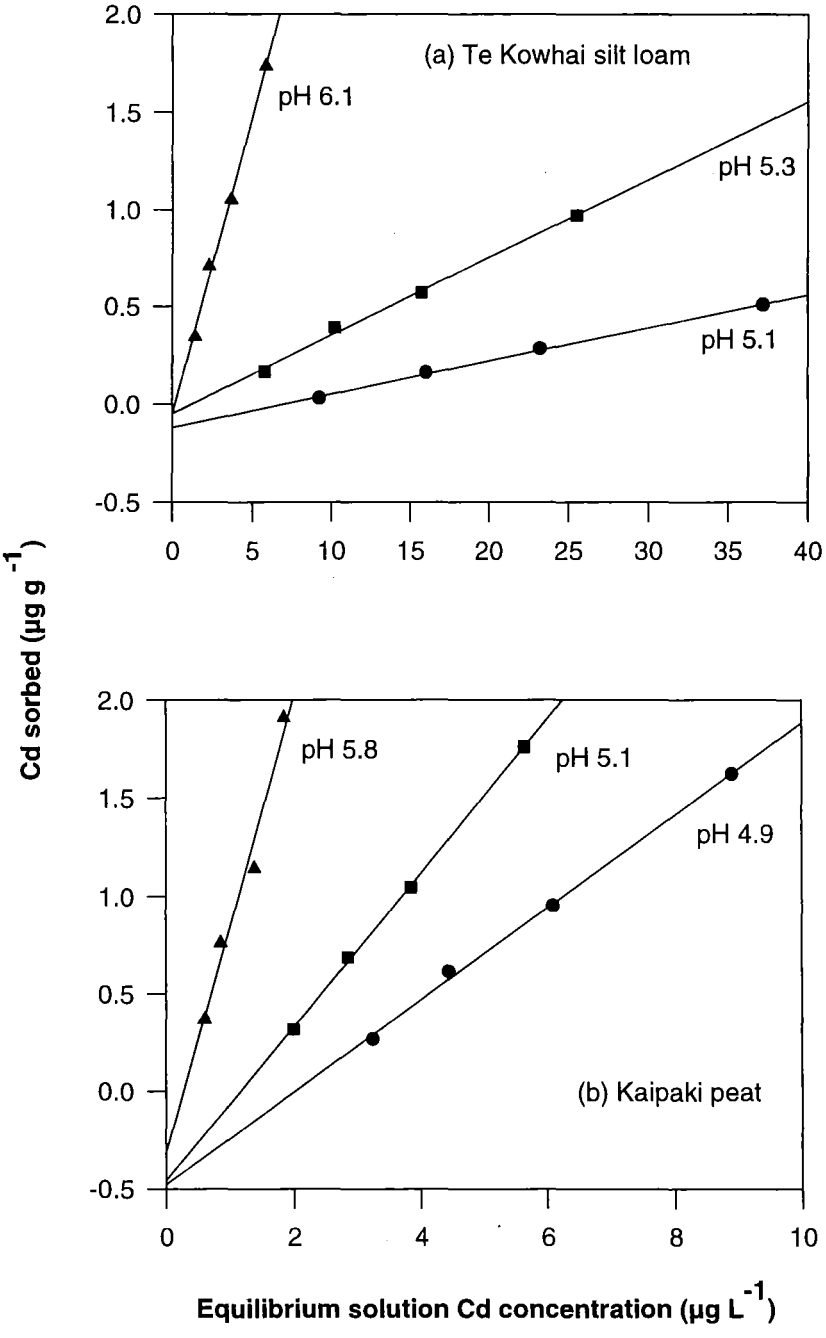


Fig. 4.2 Effect of pH on the sorption of Cd by (a) Te Kowhai silt loam and (b) Kaipaki peat.

Table 4.6 Effect of soil pH on percentage (%) of Cd sorbed and desorbed

Soil	pH	% Cd sorbed [A]	% Added Cd [B] desorbed
Te Kowhai silt loam	5.1	38.3	91.1
	5.3	50.4	97.2
	6.1	87.1	72.8
Te Kowhai humic silt loam	5.1	64.5	99.2
	5.4	78.5	69.4
	6.2	95.6	27.3
Te Rapa peaty silt loam	4.9	54.8	95.6
	5.3	72.8	81.5
	5.9	93.6	41.9
Motumaoho silty peat	5.0	85.7	59.9
	5.3	89.7	46.6
	5.9	95.6	22.3
Kaipaki peat	4.9	82.3	67.7
	5.1	88.9	52.7
	5.8	96.1	25.0
Waiotira silt loam	5.1	63.6	96.9
	5.7	84.2	62.1
	6.0	89.7	42.6

[A] Sorption from 2 μg Cd/g addition
[B] Corrected for native Cd

For all soils, the sorption isotherms had negative intercepts on the y-axis, e.g. as shown for the Te Kowhai and Kaipaki soils in Fig. 4.2. These intercept concentrations could be indicative of the amounts of "native" sorbed Cd in equilibrium with the solution phase. However, the concentrations of native Cd desorbed from the soils during 5 desorption equilibrations represented small proportions only of the intercept concentrations (Table 4.7). Initial native Cd desorption equilibrations were consistent with the linear isotherms, whereas subsequent desorption equilibrations released less Cd than would be predicted from the linear isotherms (Fig. 4.3). A similar phenomenon was reported by Boekhold *et al.* (1993) who suggested that newly added Cd interacts with different types of binding sites from the bulk of the initial Cd present in the soil. In the present study, the proportion of native sorbed Cd (as determined from the isotherm intercepts) that could be readily desorbed, generally decreased with an increasing in pH and was minimal at pHs approaching 6.0 (Table 4.7).

For all 6 soils, the effect of increasing soil pH resulted in a significant increase in Cd sorption, which is consistent with previous studies (Garcia-Miragaya and Page 1978; Christensen 1984a; Boekhold *et al.* 1993; Naidu *et al.* 1994; Taylor and Theng 1995; Lee *et al.* 1996b). Comparison of Cd sorption between soils at different pH values can be achieved by comparing sorption isotherm gradients i.e. K_d values; the Cd distribution coefficient expressing the ratio of sorbed Cd to solution Cd at equilibrium (Table 4.7). K_d values were larger than those reported in most other studies, but were within the range reported by Christensen (1989) for 63 Danish soils, in which a strong relationship between Cd distribution coefficients (K_d) and soil pH were observed.

Table 4.7 Linear isotherm intercepts, K_d values and native Cd desorbed as a percentage of the isotherm intercept value

Soil	pH	K_d ($L\ g^{-1}$)	Intercept ($\mu g\ Cd\ g^{-1}$ soil)	Native Cd desorbed (% of the intercept)
Te Kowhai silt loam	5.1	0.016	-0.119	66.1
	5.3	0.040	-0.048	90.3
	6.1	0.305	-0.051	4.6
Te Kowhai humic silt loam	5.1	0.081	-0.105	25.2
	5.4	0.154	-0.096	18.3
	6.2	1.147	-0.057	0.0
Te Rapa peaty silt loam	4.9	0.045	-0.211	29.1
	5.3	0.108	-0.125	30.9
	5.9	0.595	-0.213	1.2
Motumaoho silty peat	5.0	0.385	-0.916	2.9
	5.3	0.451	-0.513	3.5
	5.9	0.895	-0.029	0.0
Kaipaki peat	4.9	0.236	-0.476	6.4
	5.1	0.392	-0.454	2.9
	5.8	1.163	-0.314	0.0
Waiotira silt loam	5.1	0.091	-0.321	11.6
	5.7	0.251	-0.303	10.6
	6.0	0.348	-0.071	2.1

Cadmium sorption data were also well described by a linearised Freundlich sorption equation:

$$\log x/m = \log K + 1/n \log C \qquad (1)$$

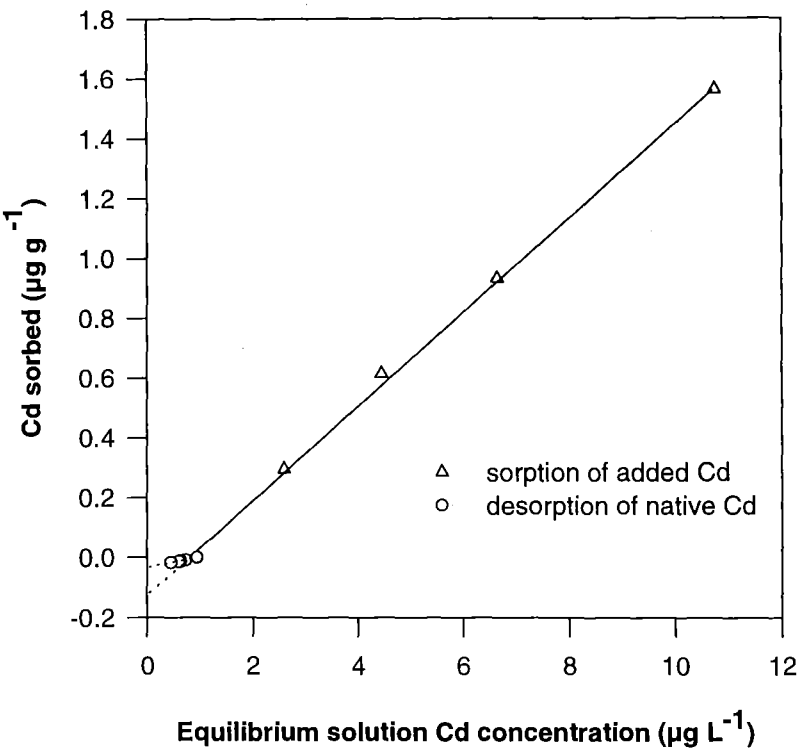


Fig. 4.3 Cadmium sorption and native Cd desorption for Te Kowhai humic silt loam pH 5.4.

where *x/m* is the Cd adsorbed (μg g^{-1}), *C* is the equilibrium Cd concentration (μg mL^{-1}) and log *K* and 1/n are empirical constants. Cadmium sorption has been described by Freundlich isotherms in other studies (O'Connor *et al.* 1984; Chardon 1984; Christensen 1984a; Kookana *et al.* 1994). The Freundlich *K* constant describes the partitioning of a metal between solid and liquid phases, and implies Cd sorptive capacity. Largest *K* values were obtained for samples high in organic carbon and at highest soil pHs e.g. Motumaoho silty peat (Table 4.8). In general the *K* values are much greater compared to most other studies, this is attributed to the relatively high organic carbon values encountered in the soils studied. The log *K* values determined are similar however to the results of Hooda and Alloway (1994) for sewage sludge amended soils.

Table 4.8 Freundlich isotherm parameters for Cd sorption

Soil	pH	log K ($mL\ g^{-1}$)	1/n
Te Kowhai silt loam	5.1	2.69	2.00
	5.3	1.88	1.18
	6.1	2.73	1.11
Te Kowhai humic silt loam	5.1	2.37	1.27
	5.4	2.51	1.16
	6.2	2.95	0.95
Te Rapa peaty silt loam	4.9	2.65	1.67
	5.3	2.68	1.37
	5.9	3.39	1.25
Motumaoho silty peat	5.0	5.53	2.44
	5.3	4.19	1.69
	5.9	3.37	1.14
Kaipaki peat	4.9	3.82	1.75
	5.1	3.93	1.64
	5.8	4.01	1.37
Waiotira silt loam	5.1	3.51	1.69
	5.7	3.32	1.47
	6.0	2.49	0.99

The effect of pH on metal cation sorption is predominantly a function of changes in the net proton charge on soil particles (Sposito 1984). The sorption capacity for Cd in the soils studied, like other metal cations, is highly pH dependent. Various models have been put forward to describe this type of sorption phenomena. These include a metal hydrolysis

model (Hodgson *et al.* 1964), metal-proton exchange model (Boekhold *et al.* 1993) and a pH dependent ion exchange model (Barrow 1984). Organic matter has been shown to have a high negative charge density, arising mainly from the dissociation of carboxyl and phenolic groups. This results in the net charge on the soil colloids becoming increasingly negative as the soil pH values increase. McBride *et al.* (1997) commented that in addition to soil pH, organic matter has an overriding importance on metal solubility in sorption experiments. This comment is supported in the present work where organic matter appears to be the most important soil component controlling sorption in the soils studied. A multiple regression model including terms for pH and total C was able to explain 87% of the variation in Cd sorption between all the soils in Table 4.1.

$$\text{Cd sorbed } (\mu g\ g^{-1}) = 0.596\ pH + 0.877 \log \text{Org. C } (\%) - 2.72 \qquad (2)$$
$$(r^2 = 0.87)$$

For the above equation both variables were highly significant ($p < 0.0001$) and quite clearly show that along with soil pH, organic carbon plays a significant role in controlling Cd sorption onto these soils.

Stevenson (1982) suggested that carboxyl groups are the group of most importance in this process, with Cd forming inner sphere complexes. The importance of organic matter in Cd sorption has also been documented by Lee *et al.* (1996b) and Kim and Fergusson (1992). Increases in Cd bound to organic matter as soil pH is increased have also been observed previously (McBride *et al.* 1981; Gerritse *et al.* 1982; Mann and Ritchie 1993). Increased competition between Cd and H^+ ions competing for the same sites at lower pHs is also likely to be an important factor in controlling Cd sorption (Garcia-Miragaya and Page 1978).

4.3.5 Added Cd desorption

Added Cd desorption data is plotted as cumulative Cd desorbed during 10 successive desorption events ($\mu g\ g^{-1}$) from that Cd initially sorbed from a 2 μg Cd g^{-1} addition. Typical examples are shown in Fig. 4.4, (data for other soils are shown in Appendix 4.3). As with desorption of native Cd, an increasing soil pH for all 6 soil samples resulted in a substantial reduction in the amount of added Cd desorbed with 10 successive equilibrations

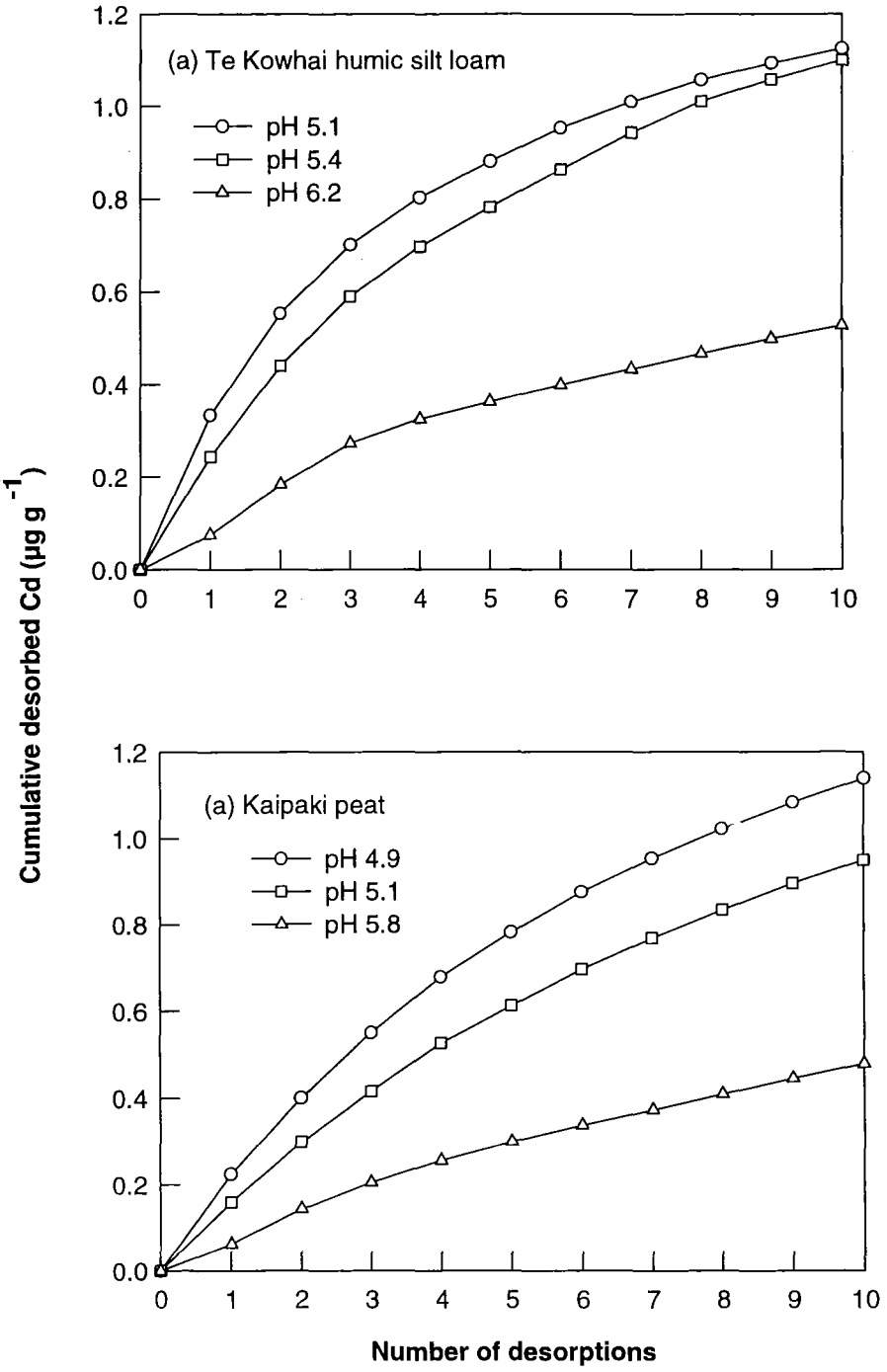


Fig. 4.4 Effect of pH on cumulative desorption of added Cd from (a) Te Kowhai humic silt loam and (b) Kaipaki peat.

in 0.01 M $Ca(NO_3)_2$ (Table 4.6). The percentage Cd desorbed from the highest concentrations sorbed, ranged from 97 to 22 % of that Cd initially sorbed. Patterns and amounts of Cd desorbed differed substantially between soils. More Cd was desorbed from samples at lowest pHs, and samples with the least amounts of organic carbon e.g. Te Kowhai silt loam, whereas samples with large amounts of organic carbon and high pH desorbed the least Cd e.g. Kaipaki peat. For example, with the Te Kowhai Humic silt loam an increase from pH 5.1 to 6.2 resulted in a 72% reduction in desorption whereas with the Kaipaki peat an increase from pH 4.9 to 5.8 resulted in 44% reduction in desorption (Table 4.6). The hysteresis between sorption and desorption isotherms becomes greater with increasing soil pH (Fig. 4.5). Data for other soils are shown in Appendix 4.4.

The results of the present study are consistent with the findings of Jarvis and Jones (1980), Christensen (1984b), Tiller *et al.* (1984a) and Pardo (1997) who found Cd desorption to be very sensitive to soil pH. This reduction in desorption with increased pH has also been found in studies involving other cations e.g. copper (Padmanabham 1983; Cavallaro and McBride 1984; Hogg *et al.* 1993), and zinc (Stahl and James 1991; Pardo and Guadalix 1996).

Padmanabham (1983) has suggested the presence of sites of lower and higher bonding energies, corresponding to readily and less readily desorbed sites in soils. Tiller *et al.* (1984a) suggested that the presence in soils of high-affinity and low affinity sites that were strongly pH dependent. There appears to be a less readily desorbed fraction of sorbed Cd, that increases with higher pH. Thus in the soils in the present work, at lower pHs, larger amounts of Cd were desorbed during the initial desorbing events, corresponding to Cd associated with low affinity sorption sites. In contrast at higher pHs, smaller amounts of Cd was desorbed in subsequent extraction events, indicating a greater number of stronger or high affinity sorption sites.

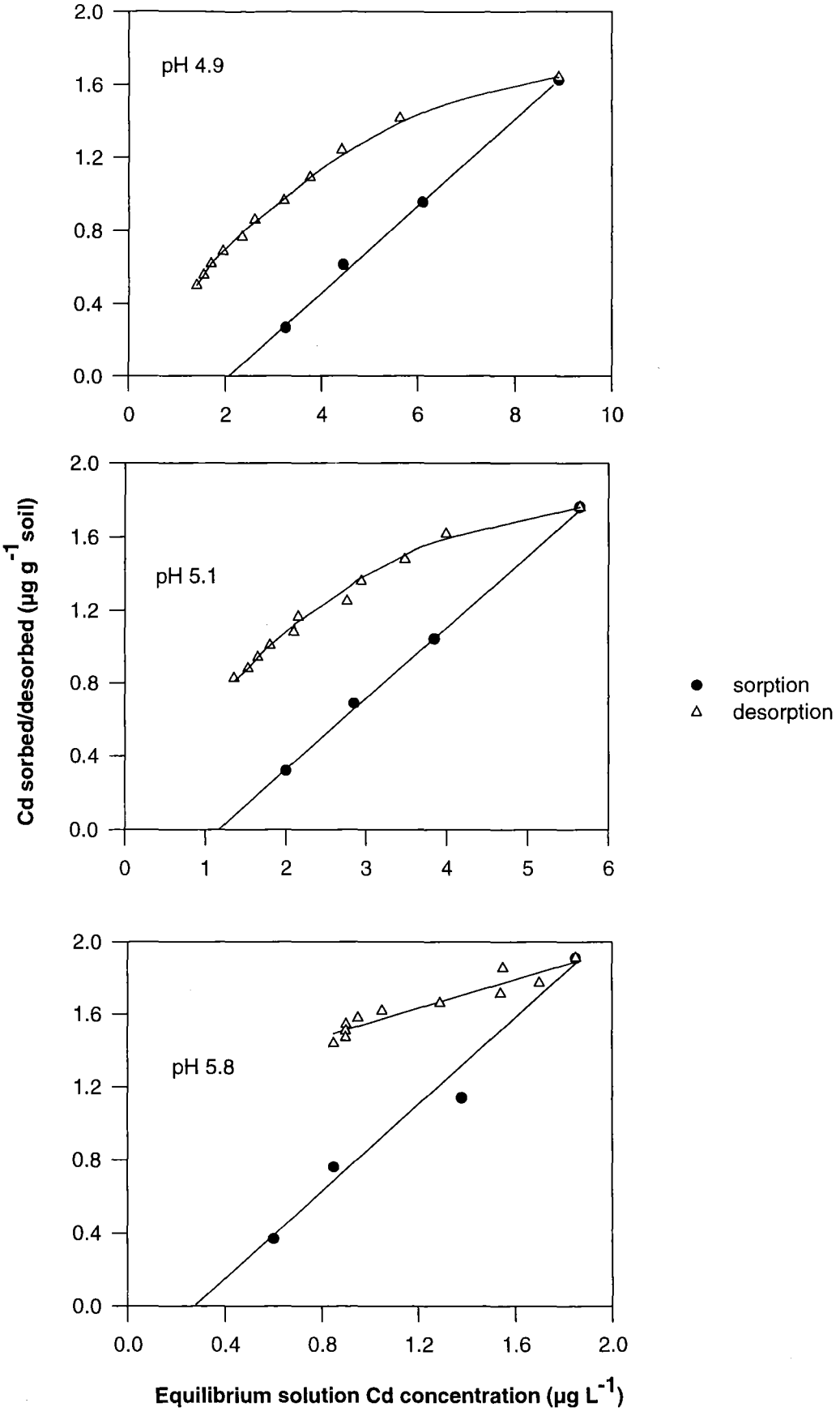


Fig. 4.5 Cadmium sorption (●) desorption (△) isotherms for the Kaipaki peat at pH 4.9, 5.1, and 5.8.

4.3.6 Contact time

Increasing the time available for sorption decreased the subsequent desorption of Cd in all 4 soils examined (Table 4.9). The Waiareka clay loam (Fig. 4.6) showed the most significant effect of contact period, with a 47% decrease in desorption with time (data for other soils are shown in Appendix 4.5). This sample has a medium organic carbon content, but contains relatively large concentrations of Fe and Al oxides, and large amounts of manganese oxides. These soil components are able to sorb Cd irreversibly (Backes *et al.* 1995). In contrast, the Takahe silt loam, displayed the least effect with a 16% decrease in desorption with time (Fig. 4.6). This soil contains relatively little Mn, Fe, and Al oxides and organic carbon (Table 4.2).

Table 4.9 Effect of contact period on cumulative Cd desorbed from soils prior treated with 2 μg g^{-1} Cd as $Cd(NO_3)_2$

	Contact period (days)		
Soil	5	30	70
Te Kuiti silt loam	2.33	1.87	1.83
Waiareka clay loam	0.48	0.23	0.23
Takahe silt loam	2.09	1.77	1.76
Temuka clay loam	1.50	1.13	1.21

Some studies have indicated the rapid sorption of metals onto soil surfaces after exposure, with little or no change with contact time (Sidle and Kardos 1977; Christensen 1984a; King 1988). In other work involving sorption of metals onto soils or soil components however, increasing the contact time between soil and sorbed trace metal has been shown to lead to decreases in the metal's subsequent ability to desorb from the soil (Kuo and Mikkelson 1980; Padmanabham 1983; Lehmann and Harter 1984; McLaren *et al.* 1986; Hogg *et al.* 1993; Ainsworth *et al.* 1994; Backes *et al.* 1995; Fischer *et al.* 1996). Such observations have been linked to processes involving solid state diffusion of ions into mineral lattice structures, especially oxides materials (Bruemmer *et al.* 1988; Ainsworth *et al.* 1994). A second explanation offered for the reduction in desorption with time may lie in the finding that there is slow redistribution of ions to more strongly bound or less accessible sorption

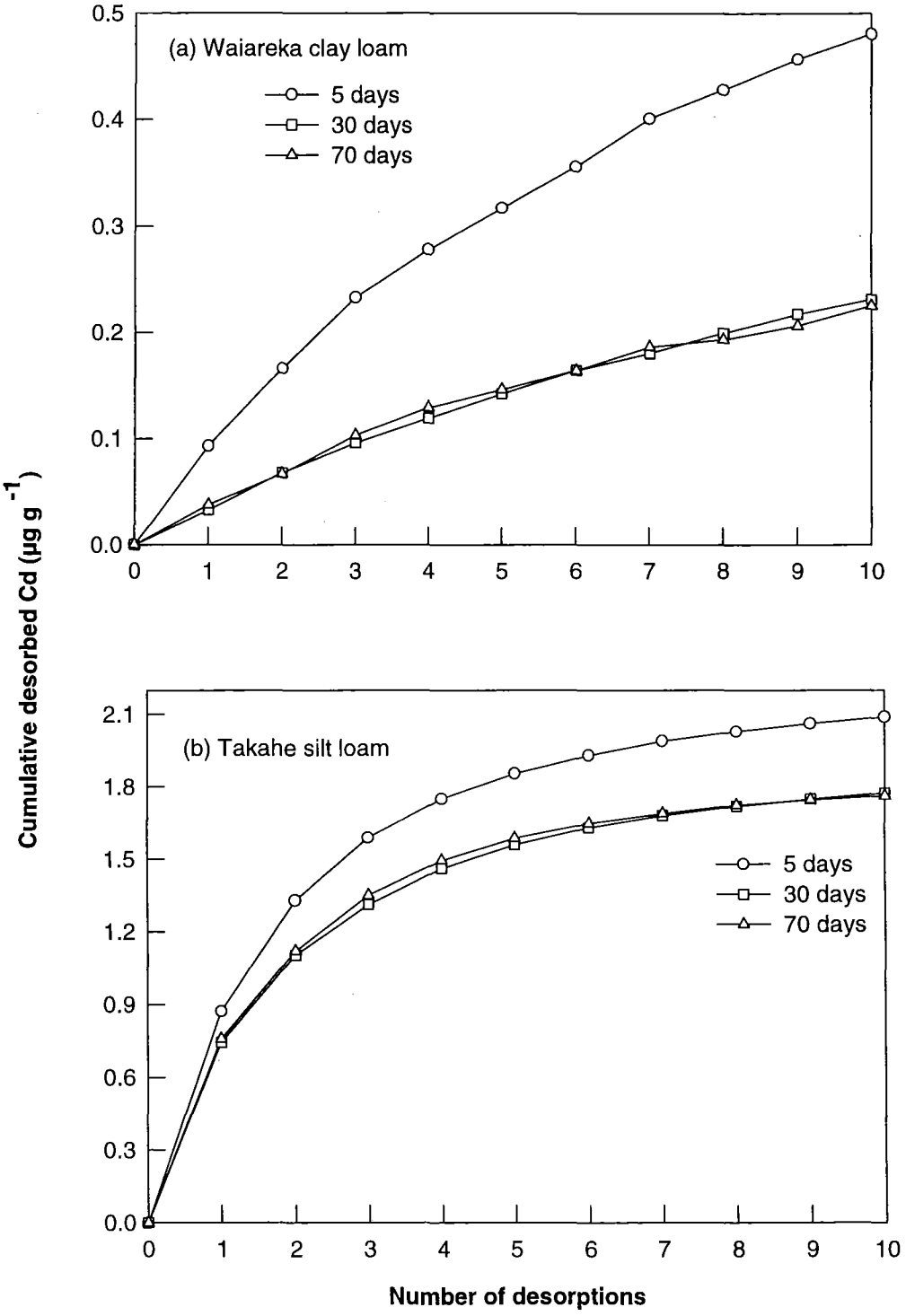


Fig. 4.6 Effect of contact time on cumulative desorption of added Cd from (a) Waiareka clay loam (b) Takahe silt loam.

sites (Mann and Ritchie 1994). This possibly involves diffusion into extremely small pores. Fischer *et al.* (1996) examining the micro-topgraphy of goethite particles found numerous wedge-shaped micropores occurred at domain boundaries on this crystal. Fischer *et al.* (1996) suggest these micropores could affect adsorption and desorption of heavy metal ions. This second idea appears plausible in the present work, where most redistribution of Cd ions has occurred within at least 30 days, possibly quicker. This change in retention of Cd with time will depend on the type of components present in the soil, and the factors that affect the retention by each soil component i.e. (pH-dependent charges).

A decrease in desorption of Cd from soil surfaces with increasing contact time may be important if there is a corresponding decrease in Cd phytoavailability. Reports on this in the literature seem to be inconclusive. For example, Eriksson (1989) and Jensen and Mosbaek (1990) showed no significant reduction in availability of Cd to plants with time. Similar results have been reported by Sparrow *et al.* (1992) and McLaughlin *et al.* (1995) for studies investigating Cd uptake in potatoes. However, in a recent study with one soil by Hamon *et al.* (1997), it was demonstrated that a significant proportion of the total Cd was unavailable for plant uptake. Since the Cd present in the soil used was derived largely from the long-term application of soluble Cd contained in superphosphate, Hamon *et al.* (1997) suggested that this could be taken as evidence for the decline in Cd availability with time. Studies by Hooda and Alloway (1993) also showed a small, but inconsistent, decline in phytoavailability with time of Cd added to soil as $Cd(NO_3)_2$. It seems likely that phytoavailability of Cd will depend very much upon the type of components present in the soil and loading or rate of application of Cd to the soil.

4.4 Conclusions

The effects of soil pH and contact time on Cd sorption and desorption for a range of New Zealand soils was investigated. For the soils examined in this study, organic carbon played a significant role in controlling Cd sorption, and sorption increased significantly with increasing pH. There was also a large concomitant decrease in Cd desorbed back into solution with increasing soil pH. It should be emphasised however, that the soils examined

all had relatively high organic carbon contents, and in other soils, components other than organic carbon may also influence Cd sorption and desorption.

An increase in contact time between the soil and added Cd also resulted in subsequent reduction in desorption of Cd into solution, which also varied with soil type. Based on the effects of soil pH and contact time it is concluded the both these processes are likely to have implications for plant available Cd, given that they control solution Cd concentrations. In practice, pastoral and other farmers should maintain soil pH levels in the target range (i.e. 5.8 - 6.0) for pasture production, and should adopt cultural practices which maintain the organic matter content of topsoils. In this way, Cd plant availability will be minimised. Additionally, provided current efforts are sustained to continue the reduction of Cd inputs into soils, the implications of the present study are that Cd already present in the soils may become less phytoavailable with time.

Chapter 5

Solubility, sorption and desorption of native and added Cd from a range of New Zealand soils in relation to soil properties

5.1 Introduction

A recent national survey of the Cd status of some NZ pastoral soils indicates that Cd has accumulated to concentrations double those of their corresponding native soils (Roberts *et al.* 1994). This accumulation of Cd has been linked to superphosphate fertiliser application, in which Cd is an impurity. It is likely that a large proportion of the added Cd is retained by the soil. Cadmium sorption varies among soil types and depends on factors such as the chemical and mineralogical characteristics of the soils and composition of the soil solution. These include pH (Garcia-Miragaya and Page 1978; Pardo 1997); cation exchange capacity (CEC) (Levi-Minzi *et al.* 1976; Zachara *et al.* 1992); organic matter (Riffaldi and Levi-Minzi 1975; Wilkens and Loch 1997; Yuan and Lavkulich 1997); soil texture (Reid and McDuffie 1981; Kim and Fergusson 1992) and Fe and Al oxides (Jarvis and Jones 1980; Tiller *et al.* 1984b).

The phytoavailability of Cd in soil is dependent upon the concentration of Cd in soil solution. Knowledge of the factors affecting the concentration of Cd dissolved in the solution phase of soils, is central to our understanding of the behaviour of Cd in the soil system (Helmke and Naidu 1996). In addition, it is also important to indentify soil factors that control the ability of soils to release Cd from its association with the solid phase into soil solution, a process likely to be controlled by desorption at the low Cd concentrations typical of New Zealand agricultural soils.

While the majority of literature is focused on the Cd sorption process, and how sorption is related to various soil properties, there is a dearth of information on the effects of soil properties on the solubility and desorption of Cd from soils. The objective of this chapter was to examine the sorption and desorption of native and applied Cd from a group of soils with more diverse chemical/physical properties than investigated in chapter 4, and to relate the Cd sorption/desorption and solubility characteristics to individual soil properties.

5.2 Materials and methods

5.2.1 Soils

Twenty-nine topsoil samples (0 - 75mm) were taken from the North and South Islands of New Zealand for this study. The soils were selected to represent a wide range of soil properties (e.g. organic matter, soil pH, free oxides and clay content) expected to influence the behaviour of soil Cd. The soil series and soil classification are listed in Table 3.1.

5.2.2 Soil preparation and analysis

All soil samples were air-dried and ground to pass through a 2 mm stainless steel sieve prior to laboratory analysis. Soil pH was measured in a water suspension using a soil:solution ratio of 1:2.5. Soil texture was determined by the pipette method (Day 1965). Total carbon content of the soils was determined by LECO CNS 2000 analyser. Total Cd was determined by a nitric acid microwave digestion method (USEPA SW 846-3051). Cation exchange capacity (CEC) was determined by ammonium acetate leaching at pH 7.0 (Blakemore *et al.* 1987). Amorphous iron (Fe) and aluminium (Al) oxides were determined by ammonium oxalate extraction (Blakemore *et al.* 1987). Crystalline Fe and Al oxides were determined by the oxalate/ascorbic acid extraction method of Shuman (1982), correcting the results for amorphous Fe and Al. Manganese oxide content was determined by extraction with 0.1 M hydroxyl-amine hydrochloride (Shuman 1982), bioavailable P (Olsen P) was determined by bicarbonate extraction (Blakemore *et al.* 1987). The properties of the experimental soils are shown in Table 5.1.

5.2.3 Soluble Cd

Soluble Cd was determined by equilibriation of soil samples (5.0 g) with 30 mL 0.01 M $Ca(NO_3)_2$. Equilibrations were carried out for 2 h at 20 °C, after which samples were centrifuged at 10 000 rpm (RCF 9, 440 *g*) for 10 minutes, filtered through a Whatman No. 42 filter paper and Cd determined in the supernatant by graphite furnace atomic absorption spectrophotometry (GFAAS) using a GBC furnace, with deuterium background correction and using a 0.1% H_3PO_4 modifier.

Table 5.1 Properties of the experimental soils

Soil	pH	Texture			Org. C	Olsen P	Total P	CEC	Mn oxides	Fe oxides		Al oxides	
		sand	silt	clay						crystal	amorp	crystal	amorp
		(%)			(%)	($\mu g\ g^{-1}$)	(%)	($cmol_c kg^{-1}$)	($\mu g\ g^{-1}$)	(%)			
1	5.0	32.4	58.7	8.7	9.6	4	0.149	6.3	74.0	0.28	0.95	0.04	2.09
2	4.9	24.9	45.3	29.8	13.0	13	0.291	9.2	620.0	0.19	0.80	0.32	3.10
3	5.2	48.0	34.4	17.7	6.7	117	0.264	10.8	162.3	0.41	0.59	0.12	0.27
4	4.8	61.6	23.4	15.0	8.3	9	0.138	8.7	246.1	0.43	0.36	0.12	0.77
5	5.2	14.2	62.2	24.6	5.5	6	0.090	14.6	50.4	0.24	0.95	0.20	0.16
6	4.9	40.2	47.7	12.2	2.4	23	0.103	4.5	31.3	0.70	0.17	0.23	0.09
7	5.0	17.2	80.7	2.1	4.7	16	0.082	9.2	161.6	0.72	0.24	0.27	0.12
8	6.1	19.3	47.2	33.4	4.9	51	0.132	22.9	338.0	0.15	0.88	0.11	0.18
9	5.5	27.9	32.8	39.3	3.6	45	0.103	11.1	56.5	0.77	0.28	0.27	0.16
10	5.4	16.1	54.5	29.4	2.6	15	0.063	11.8	113.0	0.53	0.44	0.25	0.11
11	5.4	18.9	71.2	6.3	7.4	17	0.171	10.8	170.0	0.88	0.68	0.68	2.30
12	5.1	29.5	32.5	37.9	5.2	18	0.110	9.7	54.9	0.65	0.60	0.06	0.77
13	5.3	29.5	32.5	37.9	4.8	18	0.110	9.7	54.9	0.65	0.60	0.06	0.77
14	6.1	29.5	32.5	37.9	5.1	18	0.110	9.7	54.9	0.65	0.60	0.06	0.77
15	5.1	18.9	45.3	35.8	13.2	13	0.161	19.0	39.0	0.22	0.16	0.13	1.08
16	5.4	18.9	45.3	35.8	13.4	13	0.161	19.0	39.0	0.22	0.16	0.13	1.08
17	6.2	18.9	45.3	35.8	12.7	13	0.161	19.0	39.0	0.22	0.16	0.13	1.08
18	4.9	21.3	60.4	18.3	17.3	20	0.194	19.0	28.1	0.17	0.39	0.14	1.41
19	5.3	21.3	60.4	18.3	17.1	20	0.194	19.0	28.1	0.17	0.39	0.14	1.41
20	5.9	21.3	60.4	18.3	17.7	20	0.194	19.0	28.1	0.17	0.39	0.14	1.41
21	5.0	27.1	57.0	15.9	29.7	37	0.202	33.1	40.2	0.13	0.19	0.09	0.75
22	5.3	27.1	57.0	15.9	27.8	37	0.202	33.1	40.2	0.13	0.19	0.09	0.75
23	5.9	27.1	57.0	15.9	28.6	37	0.202	33.1	40.2	0.13	0.19	0.09	0.75
24	4.9	23.1	51.6	25.3	34.2	29	0.213	30.3	12.5	0.10	0.17	0.12	0.73
25	5.1	23.1	51.6	25.3	34.3	29	0.213	30.3	12.5	0.10	0.17	0.12	0.73
26	5.8	23.1	51.6	25.3	33.1	29	0.213	30.3	12.5	0.10	0.17	0.12	0.73
27	5.1	15.3	32.4	52.4	11.4	27	0.141	23.5	65.8	0.57	0.65	0.21	0.34
28	5.7	15.3	32.4	52.4	9.2	27	0.141	23.5	65.8	0.57	0.65	0.21	0.34
29	6.1	15.3	32.4	52.4	10.4	27	0.141	23.5	65.8	0.57	0.65	0.21	0.34

5.2.4 Cadmium sorption

Cadmium sorption was determined using a batch equilibrium technique. Cadmium was added as $Cd(NO_3)_2$ to 0.5 g soil in 20 mL of a background electrolyte of 0.01 M $Ca(NO_3)_2$. Calcium nitrate was used as the supporting electrolyte to eliminate non-specific sorption of Cd, since low affinity sorption sites would be saturated by calcium ions. Initial Cd concentrations ranged between 0.01 - 0.05 μg mL^{-1}. Preliminary experiments to determine the period of equilibration showed that after 24 h there was no significant change in the amount of Cd sorbed by the soil (refer section 4.3.2.1). Therefore soil suspensions were shaken for 24 h, on a reciprocating shaker at 20 °C, after which the samples were centrifuged and the supernatant was decanted, filtered and Cd measured as described in section 5.2.3.

5.2.5 Desorption of Cd

5.2.5.1 Desorption of native Cd

Desorption of native soil Cd was determined by repeated equilibration of soil samples (5.0 g) with 30 mL of Cd-free 0.01 M $Ca(NO_3)_2$. Equilibrations were carried out for 2 h at 20 °C. This desorption period was selected as a result of a preliminary study which showed little change in the amount of Cd desorbed from the soil after a 2 h equilibration (refer section 4.3.2.2). Following equilibration, samples were centrifuged and the supernatant was decanted, filtered and Cd measured as described in section 5.2.3. The soil residue was resuspended in 30 mL of fresh, Cd-free 0.01 M $Ca(NO_3)_2$ and the procedure repeated 5 times.

5.2.5.2 Desorption of added Cd

The centrifuged residues from the highest sorption concentration i.e. 2 μg Cd g^{-1}, were weighed to determine entrained Cd, resuspended in a fresh Cd-free 20 mL volume of 0.01 M $Ca(NO_3)_2$ and equilibrated for 2 h at 20 °C. Following equilibration, samples were centrifuged and the supernatant decanted, filtered and Cd measured as in section 5.2.3. The soil residue was reweighed and resuspended in a fresh 20 mL volume of 0.01 M $Ca(NO_3)_2$, and the procedure repeated 5 times. The pH of the supernatant was determined at the end of each 2 h desorption period and was found to remain constant throughout the 5

successive desorption events, with the values 0.3-0.4 pH units less than those measured in soil:water suspensions for each soil (Table 5.1).

5.2.6 Analysis of data

The concentration of native Cd desorbed, Cd sorbed from a 2 μg Cd g^{-1} addition, and added Cd desorbed from the solid phases into solution were related to various soil properties by simple and multiple linear regressions using the minitab version 9.2 statistical package. In the case of multiple regressions, relatively high values of r^2 and low standard errors associated with the predicted regression were used as criteria of best fit. Added Cd desorbed (%) refers to the added concentration of Cd desorbed expressed as a percentage of the Cd sorbed from the 0.05 μg mL^{-1} solution.

5.3 Results and Discussion

5.3.1 Solubility of native Cd

McBride *et al.* (1997) have recently developed a semi-empirical equation from metal complexation theory, which relates metal activity of soil solutions to soil pH, organic matter and total metal content. A similar approach to Cd solubility was attempted in the present study using the semi-empirical equation provided by McBride *et al.* (1997). Water extract data was used by McBride *et al.* (1997), however these authors found that metal solubility measured by a dilute salt was strongly correlated to those measured by water extraction, thus the use of $Ca(NO_3)_2$ was considered justified.

The solubility data was subjected to linear multiple regression analysis, using a general fitting equation based on the form of equation 1, provided by McBride *et al.* (1997).

$$\text{Log}[Cd]_S = a + b\ pH + c\ \log Cd_T + d\ \log OM \qquad (1)$$

The coefficients (a, b, c, and d) can have positive or negative signs, and $[Cd]_S$ is the concentration of Cd in the 0.01 M $Ca(NO_3)_2$ extract (in units of μg l^{-1}). The quantity Cd_T represents the total Cd concentration in units of μg g^{-1} soil, whilst OM represents organic matter content of the soil in g kg^{-1}. A multiple regression model using the abovementioned terms could explain 76% of the variation in Cd solution concentration, with pH, total Cd

and OM were all highly significant ($p < 0.001$) (Equation 2). Fig 5.1 shows the degree of fit achieved for the data set, whilst equation 3 shows the equation generated by McBride *et al.* (1997) for comparison.

$$\text{Log}[Cd]_S = 7.28 - 0.89\ pH + 1.21\ \log Cd_T - 1.04\ \log OM \quad (2)$$
$$r^2 = 0.762$$

$$\text{Log}[Cd]_S = 3.62 - 0.50\ pH + 0.96\ \log Cd_T - 0.45\ \log OM \quad (3)$$
$$r^2 = 0.872$$

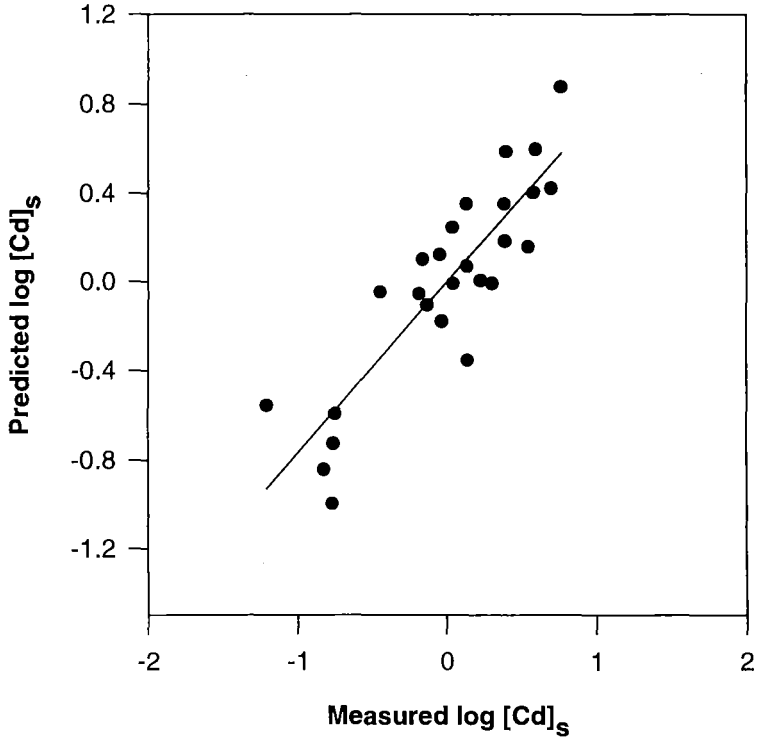


Fig. 5.1 Relationship between measured soluble Cd ($\mu g\ L^{-1}$) and predicted values.

Regression modelling revealed that although the elevations of the 2 equations were significantly different, the coefficients for pH, organic matter, and total Cd in the data sets were not significantly different from each other. In fact, the two data sets can be

successfully combined in a single multiple regression (Equation 4) which explains 81% of the variation in soluble Cd concentrations. Fig 5.2 shows the degree of fit achieved for the combined data set. The ability of a single equation to satisfactory explain soluble Cd concentrations across such a wide range of soils, and amended with either sewage sludge (McBride *et al.* 1997) or fertilisers (current study), suggests that pH, OM and total Cd are indeed the important soil properties controlling Cd solubility.

$$\text{Log}[Cd]_S = 4.33 - 0.60\,pH + 0.85 \log Cd_T - 0.45 \log OM \quad (4)$$

$$r^2 = 0.806$$

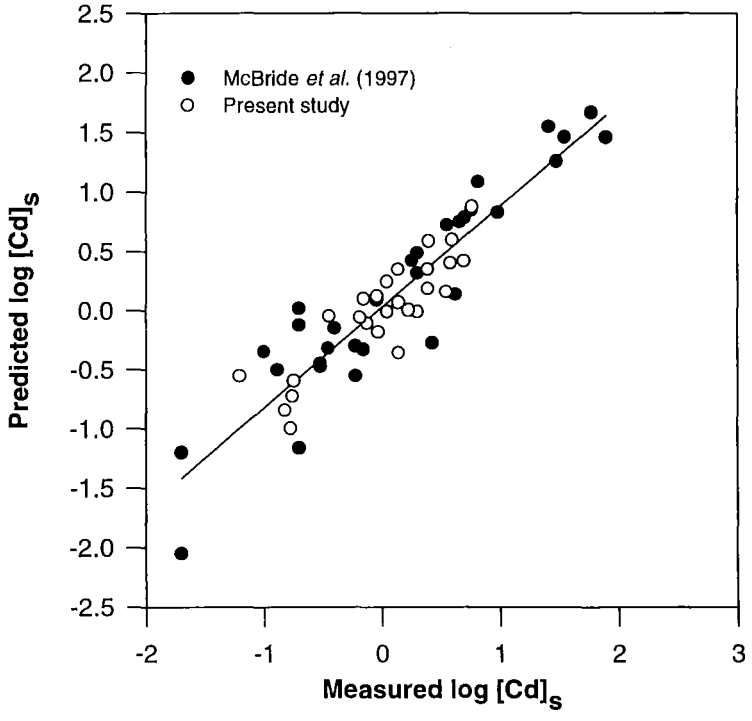


Fig. 5.2 Relationship between measured soluble Cd (μg L^{-1}) and predicted values for the data set from McBride *et al.* (1997) closed symbols and present data set open symbols.

5.3.2 Desorption of native soil Cd

The cumulative concentration of native Cd desorbed increased with the number of successive desorption events. The concentration of Cd desorbed and the patterns of desorption differed greatly between the soils. Representative examples of some soils are given in Fig 5.3. The cumulative concentration of native Cd desorbed ranged from below the detection limit for 3 samples i.e. 17, 23, 26, and up to 145.24 μg Cd kg^{-1} for soil 2 (Table 5.2).

Table 5.2 Total Cd, added Cd sorbed, native and added Cd desorbed

Soil	Total Cd (μg g^{-1})	Cumulative native Cd desorbed[A] (μg kg^{-1})	Cd sorbed[B] (μg g^{-1})	Kd Cd values (mL g^{-1})	Desorbed added Cd[A] (μg g^{-1})	Desorbed added Cd[A] (% Cd sorbed)
1	0.31	79.91	0.94	39.3	1.61	80.3
2	1.34	145.24	1.20	80.4	1.45	72.3
3	0.74	88.90	1.32	94.2	1.46	73.2
4	0.45	61.31	1.41	107.2	1.16	57.9
5	0.18	12.71	1.53	136.4	1.04	52.0
6	0.07	19.67	0.78	25.5	1.79	89.3
7	0.03	6.27	0.95	31.8	1.63	81.4
8	0.13	2.23	1.86	548.3	0.37	18.5
9	0.19	23.28	1.61	185.9	0.93	46.5
10	0.13	15.44	1.51	146.7	1.06	52.9
11	0.78	75.33	1.57	175.7	0.98	49.2
12	0.36	78.56	0.77	16.9	1.84	92.1
13	0.30	43.41	1.01	40.0	1.71	85.5
14	0.30	2.33	1.74	305.9	0.89	44.4
15	0.41	26.38	1.29	80.7	1.37	68.5
16	0.43	17.65	1.57	154.2	1.00	50.1
17	0.41	0.00	1.91	1147.5	0.38	18.9
18	0.63	61.26	1.10	45.6	1.75	87.6
19	0.62	38.89	1.46	108.1	1.25	62.7
20	0.58	2.70	1.87	595.5	0.58	29.1
21	0.97	26.15	1.71	385.1	0.82	40.9
22	0.94	17.74	1.79	451.9	0.61	30.5
23	0.91	0.00	1.91	895.9	0.27	13.5
24	1.13	30.33	1.65	236.1	0.95	47.7
25	0.99	13.43	1.78	392.2	0.69	34.5
26	0.96	0.00	1.92	1163.5	0.31	15.6
27	0.32	37.35	1.27	91.4	1.65	82.6
28	0.37	32.12	1.68	251.9	0.94	46.7
29	0.32	1.50	1.79	348.2	0.58	28.9

[A]Cumulative after 5 desorptions. [B]Sorption from a total of 2 μg Cd g^{-1} soil added

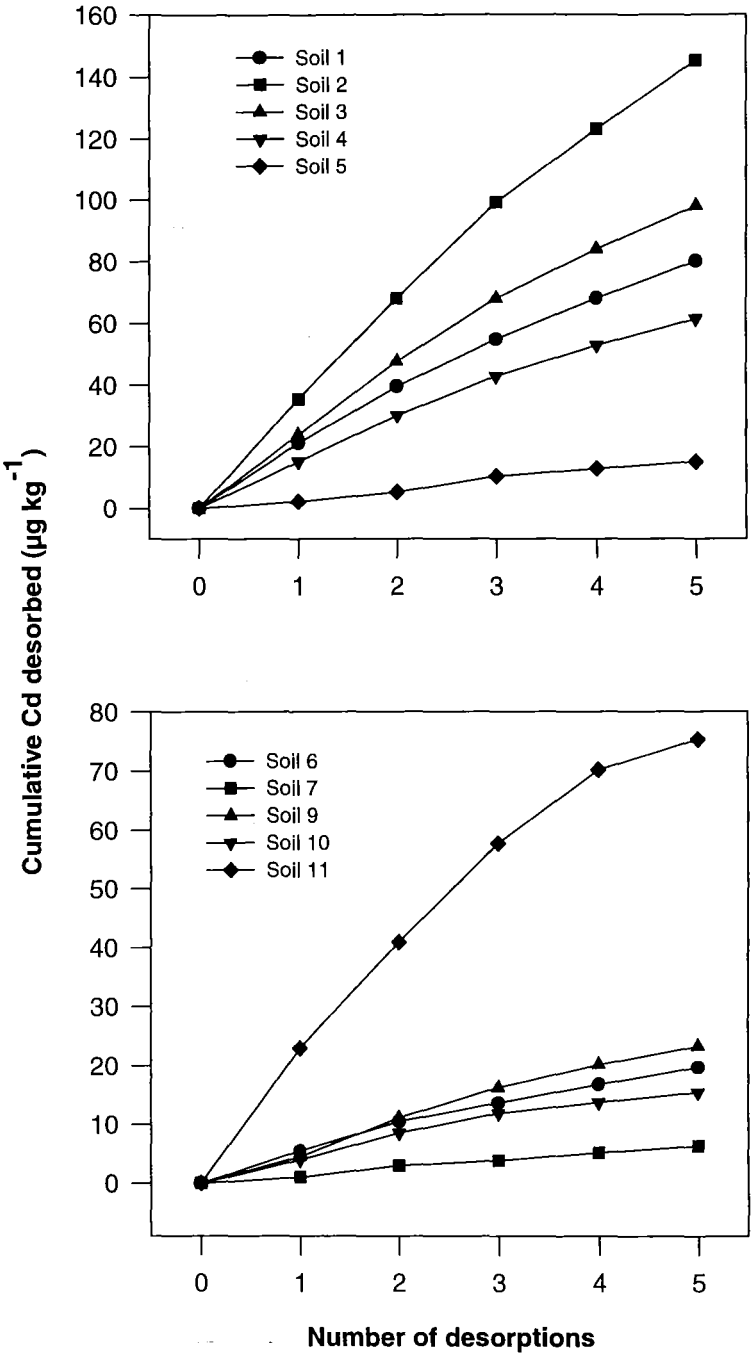


Fig. 5.3 Cumulative desorption of native Cd (µg kg^{-1}) from some New Zealand soils.

The cumulative concentrations of native Cd desorbed were found to be significantly negatively correlated with soil pH and CEC and positively correlated with Mn and amorphous Fe and Al oxides (Table 5.3). The negative relationship with soil pH and CEC indicates a decrease in the proportion of native Cd desorption as pH and CEC increases. The positive correlation with Mn oxides, and amorphous Fe and Al oxides is somewhat unusual, as these soil constituents are more usually associated with sorption of metals in soils, and therefore would more likely be negatively related to desorption of metals from soil surfaces.

Table 5.3 Correlation coefficients (*r*) between cumulative native Cd desorption and some soil properties

	pH	CEC	Org. C	Mn	Clay	Total Cd	Amor Al	Amor Fe
Native Cd desorbed	-0.57**	-0.46*	-0.20n.s	0.59**	-0.34n.s.	0.34n.s.	0.64**	0.43*

* $p < 0.05$; ** $p < 0.01$; *** $p < 0.001$; n.s., not significant

Soil pH and CEC were only able to explain between 21 to 33% of the total variation in native Cd desorption between soils (Table 5.4). In an attempt to improve prediction of native Cd desorption, multiple regressions involving 2 or more soil properties were examined. Cumulative native Cd desorption was best described by a regression model which included terms for soil pH, organic carbon and total soil Cd (Equation 5).

Cumulative native Cd desorbed = 203 - 33.3 (pH) - 3.82 (Org. C) + 115 (total Cd) (5)

$r^2 = 0.854$

This model explained 85% of the variation between soils. The degree of fit achieved for all soils in the data set using this model is shown in Fig. 5.4.

Table 5.4 Single parameter regression equations for describing Cd sorption and desorption for all soils

Regression equation			r^2
		Native Cd desorbed (μg Cd kg^{-1} soil)	
Cd desorbed	=	280 - 45.9 (pH)	0.33
	=	64.9 - 1.76 (CEC)	0.21
	=	15.4 + 33.5 (Total Cd)	0.12
	=	42.4 - 0.668 (Org. C)	0.04
		Cd sorbed (μg Cd g^{-1} soil)	
Cd sorbed	=	-1.59 + 0.571 (pH)	0.48
	=	0.990 + 0.0271 (CEC)	0.46
	=	1.25 + 0.017 (Org. C)	0.24
		Added Cd desorbed (% sorbed Cd)	
Cd desorbed	=	274 - 41.4 (pH)	0.53
	=	85.3 - 1.76 (CEC)	0.42
	=	68.9 - 0.113 (Org. C)	0.23
	=	59 .9 - 0.246 (Clay)	0.02

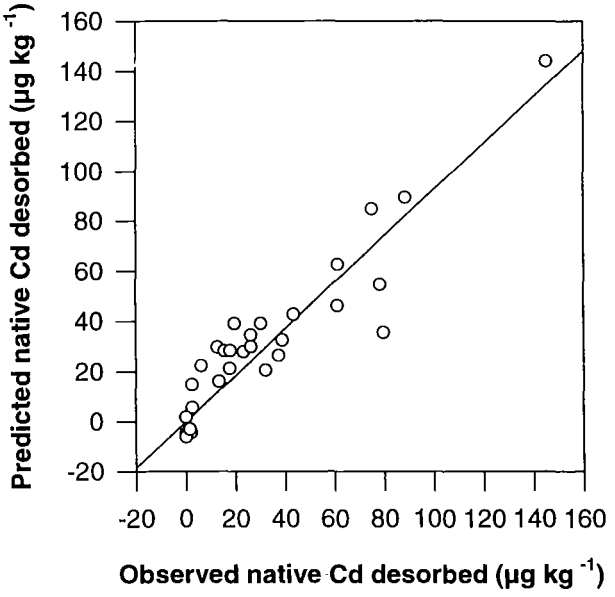


Fig. 5.4 Relationship between observed native Cd desorbed (μg kg^{-1}) and values predicted from equation 5.

Tichy *et al.* (1997) presented Cd desorption data for soils using a non-linear fitting model that contained terms for pH and organic matter content. Results indicated that pH and organic matter at high soil Cd concentration (i.e. 1.3 μg g^{-1}) had only limited effect on controlling Cd concentrations in solution, with total soil Cd being the dominant controlling factor. However, at lower soil Cd concentrations (i.e. 0.3 μg g^{-1}) as found in this study, soil pH and organic matter play a much greater role in controlling solution Cd concentrations.

5.3.3 Sorption and desorption of added soil Cd

The concentration of Cd sorbed from an initial addition of 2 μg Cd g^{-1} soil by the soils used in this study varied from 0.77 μg Cd g^{-1} for soil 12 to 1.92 μg Cd g^{-1} for soil 26 (Table 5.2). Sorption isotherms were also constructed, with some representative examples given in Fig 5.5. Sorption isotherms in all cases were linear indicating a constant partition coefficient between the soil and the solute at the low Cd concentrations used in this study. This linearity has been noted previously (Garcia-Miragaya and Page 1978; Boekhold *et al.* 1993; Gray *et al.* 1998) and has been discussed in detail in chapter 4.

Significant correlations between the concentration of Cd sorbed, and some common soil physio-chemical characteristics are given in Table 5.5. The positive relationships with pH, organic carbon and CEC indicate that with increasing organic carbon, CEC or pH there is a corresponding increase in Cd sorption. As might be expected, organic carbon and CEC were themselves significantly correlated with Cd sorption ($r = 0.843$, $p < 0.001$). These three soil characteristics have previously been shown to influence Cd sorption. For example, in a recent study by Yuan and Lavkulich (1997), a decrease in the soil organic matter content by 11 % resulted in a corresponding 62% reduction in sorption of Cd compared to the original soil. Christensen (1984a) showed that Cd sorption by sandy and loamy soils increased by a factor of three for every pH unit increase between 4 and 7.7. Rattan and Sehgal (1989) showed that electrical conductivity (EC), soil pH, and CEC are the dominant characteristics influencing the sorption of Cd for the soils they studied. Interestingly, McBride *et al.* (1997) commented that despite all the circumstantial evidence that organic matter is critical in controlling metal solubility, metal sorption experiments in soils often fail to reveal strong correlations between organic matter content metal sorption

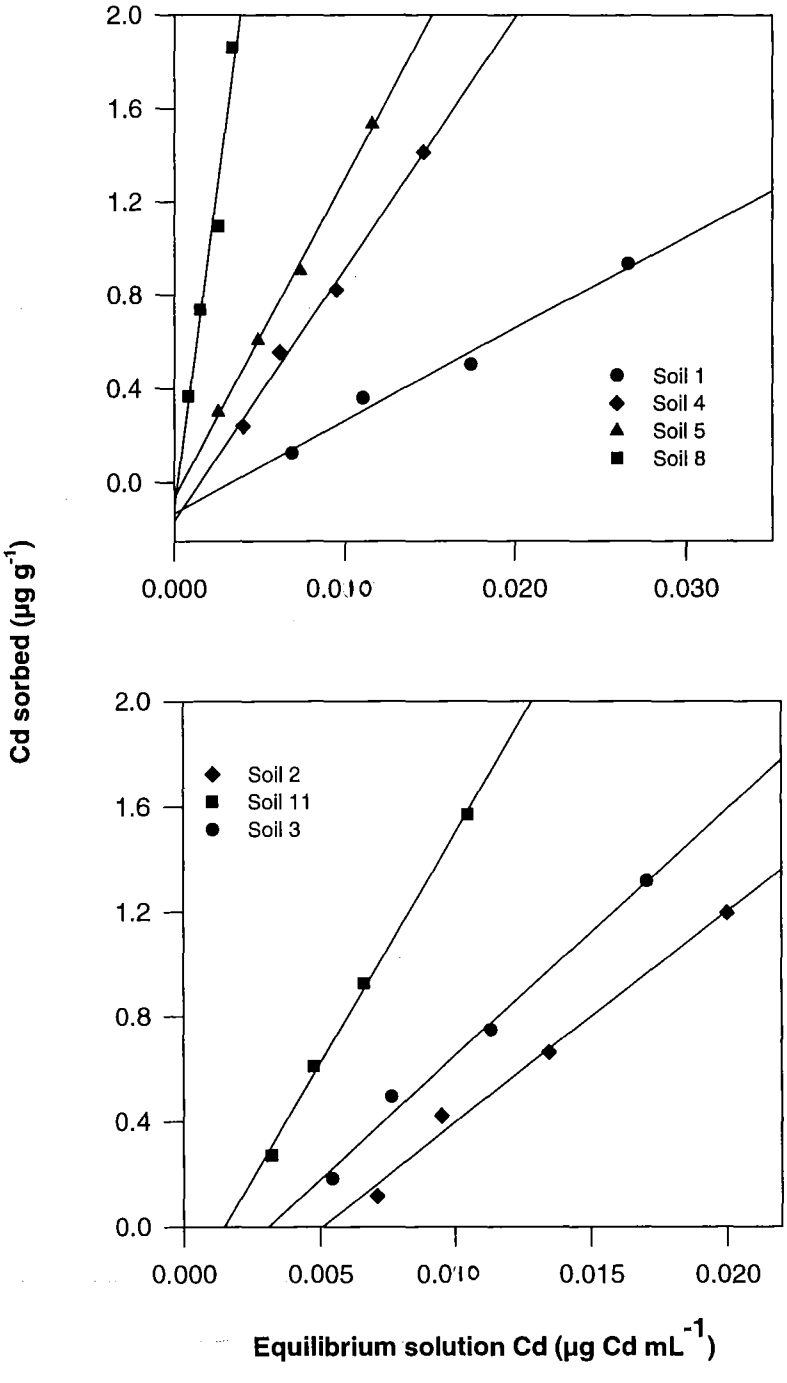


Fig. 5.5 Cadmium sorption isotherms for some New Zealand soils.

capacity. This also appears to be the case in the present investigation where organic matter alone could only explain 24% of the variation in Cd sorbed in the soils studied.

Table 5.5 Coefficients of correlation (*r*) between added Cd sorption/desorption and soil properties

	pH	CEC	Org. C	Mn	Clay
Cd sorbed	0.69***	0.68***	0.49**	-0.14n.s.	0.23n.s.
Added Cd desorbed (%)	-0.73***	-0.65***	-0.48**	0.11n.s.	-0.14n.s.

* $p < 0.05$; ** $p < 0.01$; *** $p < 0.001$; n.s., not significant

In contrast, there were no significant relationships found between Cd sorption and any of the soil oxide or textural constituents in the samples investigated. This is perhaps surprising given that clay is often an important component of soil CEC. Soil oxides (e.g. Mn, Al, Fe) have also been shown to be important sorbents for Cd in soils (Jarvis and Jones 1980; Backes *et al.* 1995). Nonetheless there have been previous studies which show no relationships between Cd sorption and soil oxide components (e.g. Wilkens and Loch 1997). Singh *et al.* (1997) found that Fe and Al oxides were not significant contributors to sorption or desorption of Zn in a similar type of study. It was suggested that the effects of Fe and Al oxides may have been masked by organic matter coatings. Furthermore, Christensen (1989) has also postulated that the dominant influence of pH does not indicate which soil components are most important in sorption of Cd, and soil oxides and clay may still be important components in sorption.

Simple linear regressions for the three soil variables most highly correlated with Cd sorption (pH, CEC and organic carbon) were able to explain only between 24 and 48% of the total variation in Cd sorption between soils (Table 5.4). However, 75% of the variation in Cd sorption between soils could be explained by a multiple regression model which includes terms for pH and organic carbon (Equation 6). This equation compares closely to sorption data from Chapter 4 using a smaller data set, which also included terms for pH and organic carbon. The degree of fit achieved for all soils in the data set using this model is shown in Fig 5.6.

Cd sorption = -1.93 + 0.589 (pH) + 0.018 (Org. C) (6)

$r^2 = 0.746$

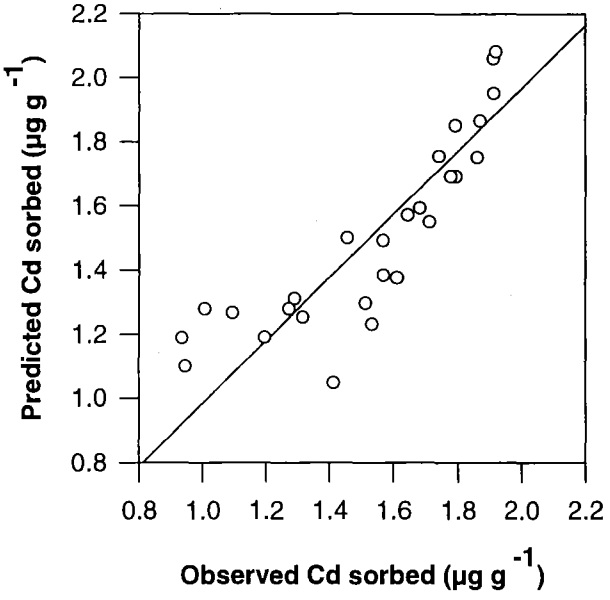


Fig. 5.6 Relationship between observed Cd sorption (µg g^{-1}) with values predicted from equation 6.

Organic carbon together with soil pH have been shown in other studies to be important factors controlling Cd sorption in soils (Kuo and Baker 1980; Gerritse and Driel 1984; Gray *et al.* 1998). King (1988) indicated that pH along with organic matter and ammonium oxalate-extractable Fe could explain 96% of the variation in Cd sorption in 13 topsoil samples. Christensen (1989) also showed that K_d values (which expresses the distribution of Cd between the soil and solute) were significantly related to soil pH and organic matter in a study of 63 soils in Denmark. Soil pH and CEC were the only soil parameters that were found to be significantly related to Cd Freundlich log K_d values for 11 soils (Buchter *et al.* 1989). McBride *et al.* (1981) correlated Cd sorption with several soil constituents which included pH and organic matter. It is interesting to note, that although on the basis of simple correlations, Cd sorption appeared to be highly correlated with CEC (Table 5.4),

this property did not appear as an important factor of the best-fitting multiple regressions examined.

5.3.4 Desorption of added Cd

The cumulative concentration of added Cd desorbed varied from 0.27 μg Cd g^{-1} for soil 23 to 1.84 μg Cd g^{-1} for soil 12. Again as with native Cd desorption, the concentrations and patterns of desorption of added Cd varied with soil type. Some representative examples are given in Fig 5.7. Of the soil Cd sorbed from an initial application of 2 μg Cd g^{-1} soil, it was observed that after 5 successive desorption events, 13.54 - 92.11 % of the sorbed Cd could be desorbed back into solution (Table 5.2). The concentration of added Cd desorbed (%) was negatively correlated with pH, organic carbon and CEC (Table 5.5). Similarly, as for native Cd desorption and Cd sorption, simple linear regression with individual soil properties were able to explain only small amounts of variation in added Cd desorption (%) between soils. The percentage ranged from between 23% for organic carbon to 53% for soil pH to (Table 5.4).

Seventy seven percent of the variation in added Cd desorption between soils could be explained by a multiple regression model including terms for pH and CEC (Equation 7). The degree of fit achieved for all soils in the data set using this model is shown in Fig 5.8.

$$\% \text{ Cd desorbed} = 261 - 34.1\,(\text{pH}) - 1.35\,(\text{CEC}) \qquad (7)$$

$$r^2 = 0.765$$

In line with the results in the present study, Jarvis and Jones (1980) and Christensen (1984b) both showed that soil pH was an important factor controlling desorption of Cd. Jarvis and Jones (1980) measured desorption for 3 soils with contrasting pH. Desorption of Cd was greatest in the sample with the lowest pH (>80%), whereas (<1.25%) Cd was desorbed from the other soils with much higher pH. Pardo (1997) similarly found desorption decreased as pH increased, and become trace at pH greater than 6. There were also distinct differences in the amounts of Cd desorbed between different soil types, and Pardo (1997) stresses that differences in desorption are not only a result of pH, but the physio-chemical characteristics of the soil matrix. Results of a study by Narwal and Singh

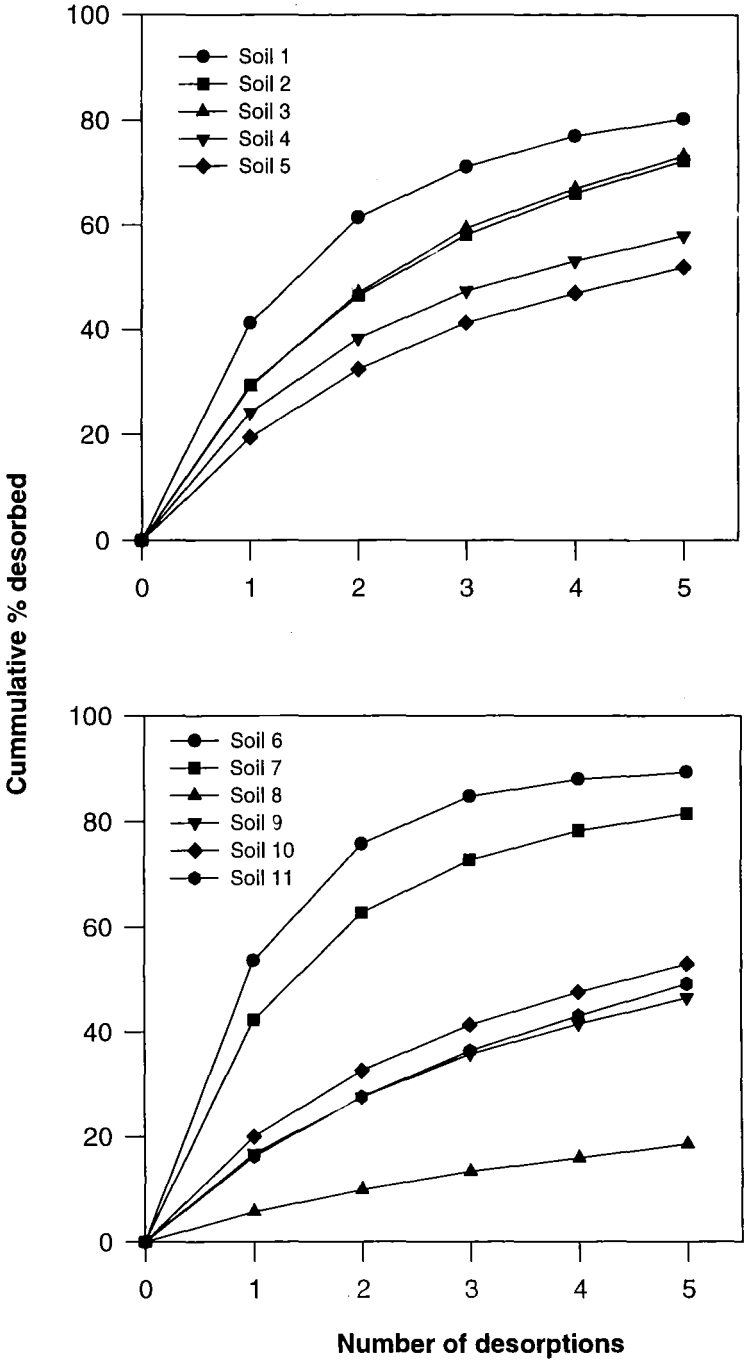


Fig. 5.7 Cumulative desorption of added Cd (μg g^{-1}) from some New Zealand soils.

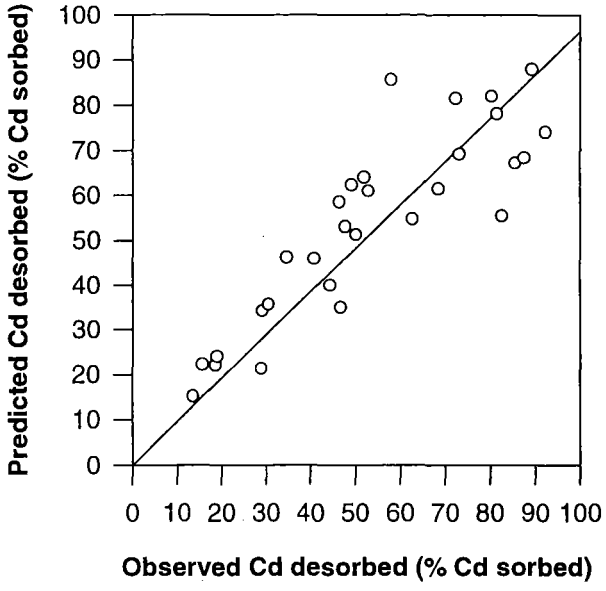


Fig. 5.8 Relationship between observed added Cd desorption (as % of Cd sorbed) with values predicted from equation 7.

(1995) indicated that desorption of added Cd was significantly greater from a sandy loam than for an alum shale, an organic soil and peat soil. This sample also had the lowest pH, organic carbon and CEC, implying these soil parameters were important for controlling Cd desorption. It appears that the results in this study are consistent with these earlier investigations, with CEC of the soil in conjunction with soil pH controlling Cd desorption in soils.

Recently, Kookana *et al.* (1997) examined the relationship between desorption of added soil Cd and soil K_d values. It was found that the amount of Cd readily exchangeable with 3 washings in 0.01 M $Ca(NO_3)_2$ decreases very rapidly with increasing K_d value for a soil. Added Cd desorbed was also plotted as a function of soil K_d values in this study (Fig 5.9). Added Cd desorbed was expressed as the fraction desorbed, which represents the ratio of Cd desorbed after 5 desorption events to the amount of added Cd sorbed. Likewise a strong log-linear relationship between Cd desorption and the soil K_d value was found to exist. The results compare very well with data calculated by Kookana *et al.* (1997) for

sorption data obtained from Tiller *et al.* (1984b), for a large number of clay seperates from Australia and Germany. It appears that the extent of desorption of Cd from soils was dependent on the affinity with which it is adsorbed. This appears logical given that similar soil properties control both sorption and desorption of Cd.

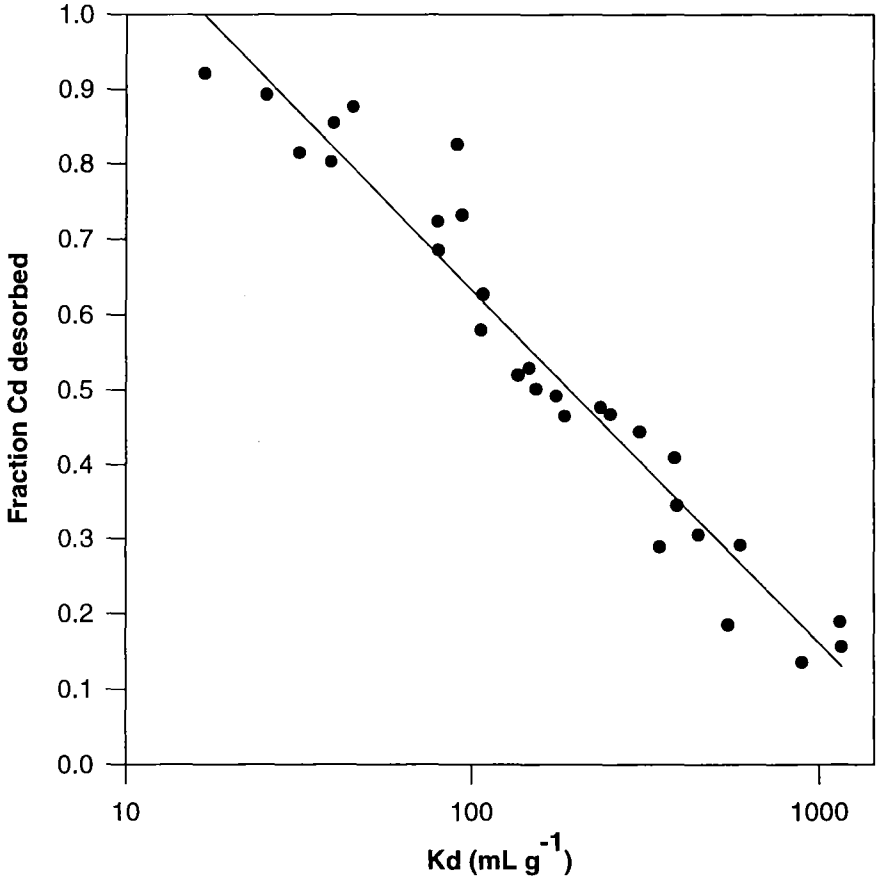


Fig. 5.9 Relationship between log Kd and desorption of Cd from soils.

5.4 Conclusions

The concentrations of soluble Cd, concentrations and patterns of native soil Cd desorbed, and added Cd sorbed and desorbed varied greatly between the 29 soils studied. Correlation analysis revealed that pH was the most dominant soil variable affecting solubility, sorption

or desorption of native and added Cd. However, organic carbon, CEC and total soil Cd were also found to be important. Multiple regression analysis showed that Cd solubility was related to soil pH, organic carbon and total Cd, which explained 76% of the variability between soils. It was found that when data from the present study was combined into a single multiple regression with data for very different soils, the equation generated could explain 81% of the variation in soluble Cd concentrations. This reinforces the importance of pH, organic carbon, and total Cd controlling Cd solubility. Simple linear regression analysis could at best explain (53%) of the total variation in Cd sorption or desorption from the different soils. Multiple regression analysis showed that native Cd desorption was related to pH, organic carbon and total Cd, which explained 85% of the variability between soils. For sorption of Cd, (from 2 μg Cd g^{-1} soil added), pH and organic carbon explained 75% of the variability between soils. However, for added Cd desorption (%), pH and CEC explained 77% of the variability. It is clear that the combined effects of a range of soil properties control the solubility, sorption and/or desorption of Cd in soils. The fraction of potentially desorbable added Cd in soils could also be predicted from the sorption capacity of a soil i.e. a soils K_d value. This could be have potential value for assessing the mobility of Cd in soil and its likely phytoavailability.

Chapter 6

Cadmium Phytoavailability in some New Zealand Soils

6.1 Introduction

Cadmium (Cd) is considered an important environmental soil pollutant as it is readily adsorbed by plants and has the potential to enter the human food chain (Chang *et al.* 1983). The uptake of cadmium in plants has been shown to be influenced by a wide range of soil and plant variables. These include soil pH (Jackson and Alloway 1991; Guttormsen *et al.* 1995), soil organic matter (MacLean 1976; He and Singh 1993a), soil salinity (Bingham *et al.* 1986; McLaughlin *et al.* 1994a), total soil Cd (Lund *et al.* 1981), micro and macronutrients (Smilde *et al.* 1992; Oliver *et al.* 1994; Sparrow *et al.* 1994; Grant *et al.* 1996) and plant species and cultivars (McLaughlin *et al.* 1994b; Oliver *et al.* 1995; Hamon *et al.* 1997).

Numerous laboratory methods have been proposed and evaluated to measure the phytoavailability of soil Cd, involving extraction of soil with a range of chemical reagents. These have included 0.01 M $CaCl_2$ (Whitten and Ritchie 1991), 0.05 M $CaCl_2$ (Jackson and Alloway 1991), 0.1 M $CaCl_2$ (Smilde *et al.* 1992), 1 M NH_4NO_3 (Symeonides and McRae 1977), 1M NH_4Cl (Krishnamuriti *et al.* 1995b), 0.05 M $Ca(NO_3)_2$ (Jing and Logan 1992), 1 M NH_4OAc (John 1972), 0.005 M DTPA (Street *et al.* 1978), 0.05 M EDTA (Jackson and Alloway 1991), 0.5 N CH_3COOH (Haq *et al.* 1980) and 1 N HCl (Lagerwerff 1971).

The majority of studies examining the relationship between soil Cd and plant uptake have been carried out on soils to which Cd in the form of soluble inorganic salts had been added (Street *et al.* 1978; Brams and Anthony 1988; Eriksson 1989; Xue and Harrison 1991; Han and Lee 1996), or using soils which have been contaminated with Cd from sewage sludge application (Haq *et al.* 1980; Alloway *et al.* 1990; Jackson and Alloway 1991; Jing and Logan 1992). Cadmium added as soluble salts or in sludge often behave differently to Cd added to the soil in a fertiliser. It has been documented for example that if all factors remain constant, plant uptake of Cd was higher when Cd was added to soil as a metal salt

e.g. $Cd(NO_3)_2$ compared to Cd in sewage sludge (Bell *et al.* 1991; Hooda and Alloway 1993). In addition, studies developing soil tests for plant available Cd have often been undertaken at very high Cd concentrations, in some cases ranging from 50 to 100 $\mu g\ g^{-1}$ (Symeonides and McRae 1977; Lee and Zheng 1993). As a consequence, these studies have only limited relevance to New Zealand agricultural soils, where soil Cd has for the most part accumulated slowly through the use of phosphate fertilisers in which Cd is an impurity, to concentrations ranging between (0.04 - 1.53 $\mu g\ g^{-1}$) (Roberts *et al.* 1994).

Therefore, the aims of this study were to evaluate the suitability of a number of commonly used soil extractants to predict plant uptake of Cd from a range of contrasting New Zealand soils at low Cd concentrations. Soil Cd having been derived either from the soil parent material, or Cd which has accumulated in the soil from the application of phosphate fertiliser. Another aim of the study was to investigate Cd uptake by several vegetable, cereal and pasture plants in relation to different soil types.

6.2 Materials and methods

Ten bulk topsoil samples (0-150 mm), which differ substantially in their total Cd content, chemical and physical properties were selected for a pot experiment (Table 6.1). The samples were ground moist to pass through a 4 mm stainless steel sieve, and a subsample taken. The subsamples were air-dried and ground to pass through a 2 mm stainless steel sieve prior to laboratory analysis. Soil pH was measured in a water suspension using a soil:solution ratio of 1:2.5. Soil texture was determined by the pipette method described by Day (1965). Total carbon content in the soils was determined by LECO CNS 2000 analyser. Total Cd was determined by a nitric acid microwave digestion method (USEPA SW 846-3051). Cation exchange capacity (CEC) was determined by ammonium acetate leaching at pH 7.0 (Blakemore *et al.* 1987). Amorphous iron (Fe) and aluminium (Al) oxides were determined by ammonium oxalate extraction (Blakemore *et al.* 1987). Crystalline Fe and Al oxides were determined by the oxalate/ascorbic acid extraction method of Shuman (1982), correcting the results for amorphous Fe and Al. Manganese oxide content was determined by extraction with 0.1 M hydroxyl-amine hydrochloride (Shuman 1982). Bioavailable P (Olsen P) was determined by bicarbonate extraction and total P was determined by NaOH fusion (Blakemore *et al.* 1987).

Table 6.1 Selected properties of the soils used for pot trial

Soil type	pH	sand	silt	clay	Org.	Total P	Olsen P	CEC	Mn	Fe		Al		Total Cd
										crystal	amorp	crystal	amorp	
		(%)					($\mu g\ P\ g^{-1}$)	($cmol_c kg^{-1}$)	($\mu g\ g^{-1}$)	(%)				($\mu g\ Cd\ g^{-1}$)
Ohura	5.0	32.4	58.9	8.7	9.6	0.149	4	6.3	74.0	0.28	0.95	0.04	2.09	0.31
Te Kuiti	4.9	24.9	45.3	29.8	13.0	0.291	13	9.2	620.0	0.19	0.80	0.32	3.10	1.34
Whakatane	5.2	47.9	34.4	17.7	6.7	0.264	117	10.8	162.3	0.41	0.59	0.12	0.27	0.74
Taupo	4.8	61.6	23.4	15.0	8.3	0.138	9	8.7	246.1	0.43	0.36	0.12	0.77	0.45
Temuka	5.2	14.2	61.2	24.6	5.5	0.085	6	14.6	50.4	0.24	0.95	0.20	0.16	0.18
Waimakariri	4.9	40.2	47.7	12.2	2.4	0.103	23	4.5	31.3	0.70	0.17	0.23	0.09	0.07
Summit	5.0	17.2	80.7	2.1	4.7	0.082	16	9.2	161.6	0.72	0.24	0.27	0.12	0.03
Waiareka	6.1	19.3	17.2	33.4	4.9	0.132	51	22.9	338.0	0.15	0.88	0.11	0.18	0.13
Tai Tapu	5.5	27.9	32.8	39.3	3.6	0.103	45	11.1	56.5	0.77	0.28	0.27	0.16	0.19
Temuka	5.4	16.1	54.5	29.4	2.6	0.063	15	11.8	113.0	0.53	0.44	0.25	0.11	0.13

6.2.1 Pot trial

Approximately 2 kg of the field moist < 4 mm sieved soil was weighed into plastic pots lined with perforated polythene plastic bags. A basal nutrient solution containing NH_4NO_3, $CaH_4(PO_4)_2.H_2O$, K_2HPO_4, K_2SO_4, $MgSO_4.H_2O$ which supplied the equivalent of 100, 40, 60, 17, 10 kg^{-1} ha^{-1} of N, P, K, S and Mg respectively, was applied to each pot at the start of the trial (25 mL pot^{-1}), with a second application after three weeks. All fertiliser applied was analytical grade (AR). Soils were made up to approximately 75 % field capacity moisture content and these weights were maintained during the trial by the addition of deionised water. Nine different species were grown: carrot (*Daucus carota* L.), cabbage (*Brassica oleracea* var *capitata* L.), lettuce (*Lactuca sativa* L.), wheat (*Triticum aestivum* L.), barley (*Hordeum vulgare* L.), maize (*Zea mays* L.), ryegrass (*Lolium perenne* L.), white clover (*Trifolium repens* L.) and lucerne (*Medicago sativa* L.). Eight wheat, barley, and maize seeds were sown per pot, and two weeks after germination, thinned to six plants. Carrot was oversown at 0.4 g of seed per pot and thinned to approximately 15 plants per pot two weeks after germination. Lettuce and cabbage were oversown at 10 seeds per pot and thinned to four plants per pot after two weeks. Pasture species were sown on weight basis, at 0.4 g per pot. The tops of the pots were initially covered with newspaper until germination of the seeds had taken place. Each crop was replicated in triplicate, and the pots arranged randomly in a glasshouse. Above ground parts of each plant, as well as carrot roots were harvested and analysed for Cd content. Clover, ryegrass, wheat and barley were harvested twice throughout the trial.
(Growing times for each plant species are given in Appendix 6.2)

6.2.2 Plant analysis

Plants were harvested at 10 mm above soil height with stainless steel scissors, shredded and dried at 65 °C. The dried sample was finely ground using a stainless steel roller. Subsamples of ground plant material (0.5g) were digested in 10 mL 69% Aristar grade nitric acid and heated on a digestion block up to 140 °C over a period of 7 h. The digest was then made up to 20 mL with deionised water and filtered through a Whatman No. 42 paper filter paper. Duplicate analysis of all the plant samples were made together with reagent blanks. Cadmium was determined in the digests by graphite furnace atomic absorption spectrophotometry (GFAAS) with a deuterium background correction and 0.1 % H_3PO_4 acid was used as a modifier.

6.2.3 Soil extractions

Eight extractants were selected to assess Cd phytoavailability in the present study (Table 6.2). The extraction procedures, i.e. extraction time, and soil to solution ratios were generally the same as those recommended by the referenced investigators (Table 6.2). In order to eliminate potential matrix effects of salts in the extracting solutions during analysis, Cd standards were prepared in the respective salt solution using AR chemicals. Cadmium in $CaCl_2$ extracts was complexed with APDC and extracted into MIBK prior to analysis, as outlined in Chapter 3. Cadmium was determined in the extracts by graphite furnace atomic absorption spectrophotometry (GFAAS) with a deuterium background correction. All analyses were carried out in triplicate, and data presented represents the mean values of the triplicate determination.

Table 6.2 Methods of assessing phytoavailable Cd in soil

Extractant	Reference	Soil/solution ratio	Time of extraction (h)
0.05 M $Ca(NO_3)_2$	Jing and Logan (1992)	1:10	16 h
1 M NH_4NO_3	Symeonides and McRae (1977)	1:10	1 h
0.01 M $CaCl_2$	Whitten and Ritchie (1991)	1:5	16 h
0.05 M $CaCl_2$	Novozamsky *et al.* (1993)	1:10	0.3 h
1 M NH_4OAc	Symeonides and McRae (1977)	1:10	1 h
1 M NH_4Cl	Krishnamurti *et al.* (1995b)	1:6	16 h
0.04 M EDTA	McLaren *et al.* (1984)	1:4	2 h
0.05 M AAAc-EDTA	Lakanen and Ervio (1971)	1:10	1 h

6.2.4 Statistical methods

Correlation and regression analysis was performed using the Minitab version 9.2 statistical package.

6.3 Results and discussion

6.3.1 Soils

The total Cd concentrations of the soils under investigation varied widely from 0.03 μg g^{-1} for the Summit soil to 1.34 μg g^{-1} for the Te Kuiti soil (Table 6.1). These values lie within the range for total Cd in pastoral soils in New Zealand as reported by Roberts *et al.* (1994). Other soil properties, which have been previously shown to influence plant uptake of Cd

also varied such as clay content, oxide content, organic carbon content, pH and CEC. Total Cd was significantly correlated to total phosphorus ($r = 0.93$, $p < 0.0001$), which indicates that the Cd in the soils studied was likely to be mainly derived from superphosphate fertiliser application.

6.3.2 Soil extractrants

The concentrations of Cd extracted from individual soils by the various extraction methods investigated are shown in Table 6.3. The concentration of Cd extracted from the 10 soils studied varied greatly, depending on the reagent used. For example, using 0.04 M EDTA, the largest concentration of Cd was extracted from the Whakatane soil (427.7 μg kg^{-1}), and the least by the Summit soil (11.6 μg kg^{-1}). However, using 0.01 M $CaCl_2$, the largest concentration of Cd was extracted from the Te Kuiti soil (33.2 μg kg^{-1}), whereas the least was extracted from Waiareka soil (1.1 μg kg^{-1}). A comparison of the mean concentrations of Cd extracted shows that values varied by an order of magnitude, ranging from 16.8 μg kg^{-1} for 0.01 M $CaCl_2$ to 174.4 μg kg^{-1} for AAAc-EDTA. For most soils, the concentration of Cd extracted were in the order: 0.05 M AAAc-EDTA > 0.04 M EDTA > 1 M NH_4Cl > 0.05 M $CaCl_2$ > 1 M NH_4OAc > 0.05 M $Ca(NO_3)_2$ > 1 M NH_4NO_3 > 0.01 M $CaCl_2$. As expected the buffered, chelate-based extractant AAAc-EDTA (pH 4.65), and EDTA (pH 6.0) extracted significantly greater amounts of Cd that did the unbuffered low ionic strength extractants such as 1 M NH_4NO_3 and 0.01 M $CaCl_2$. This type of relationship for Cd extraction from soil has been previously reported by other researchers (Symeonides and McRae 1977; He and Singh 1993a; Krishnamurti *et al.* 1995b; Andrewes *et al.* 1996). For example Mench *et al.* (1997) showed that 0.05 M EDTA-ammonium could extract 30 - 100% of the total Cd concentration in 16 soils studied, whereas 0.1 M $Ca(NO_3)_2$ could only extract 0.02 - 26% of the total Cd concentration. In addition to the extractants listed, 0.1 M $NaNO_3$ was also investigated. However the concentrations of Cd extracted were below the detection limit of the GFAAS. Sauerbeck and Styperek (1985), also found that $NaNO_3$ as an extractant was inappropriate, especially for neutral soils at soil Cd concentrations less than 2 μg g^{-1}. For this reason, Sauerbeck and Styperek (1985) replaced 0.1 M $NaNO_3$ with 0.05 or 0.1 M $CaCl_2$.

Table 6.3 Mean concentration of Cd (μg kg^{-1}) extracted from 10 different soils using different chemical extractants

Soil	0.01 M CaCl2	1 M NH_4NO_3	0.05 M $Ca(NO_3)_2$	1 M NH_4OAc	0.05 M CaCl2	1 M NH_4Cl	0.04 M EDTA	0.05 M AAAc
Ohura	18.37	31.2	44.13	52.51	63.45	185.8	130.3	132.1
Te Kuiti	33.20	63.9	85.50	149.27	130.77	372.1	404.8	590.8
Whakatane	21.33	40.4	80.98	171.2	163.87	230.3	427.7	428.3
Taupo	15.51	24.6	43.45	65.7	74.59	192.4	199.0	231.2
Temuka 1	3.46	6.8	9.24	18.1	31.50	52.5	65.4	55.0
Rakaia	5.92	6.2	11.02	12.3	21.47	31.5	24.6	23.5
Summit	1.45	2.8	2.88	3.8	8.05	10.0	11.6	9.1
Waiareka	1.10	1.5	3.54	13.3	9.66	24.4	65.1	52.9
Tai Tapu	3.77	8.5	14.16	44.6	44.36	70.8	137.8	139.0
Temuka 2	3.40	5.9	12.60	26.2	34.24	49.2	99.0	82.5
min	1.1	1.5	2.9	3.8	8.1	10.6	11.6	9.1
max	33.2	63.9	85.5	171.2	163.9	372.1	427.7	590.8
mean	16.8	18.9	30.9	55.7	58.2	121.9	156.4	174.4

The correlation coefficients of the relationships between Cd extracted by the various extractants indicate all extractants were significantly inter-related (Table 6.4). The highest correlation was found between 0.04 M EDTA and 1 M NH_4OAc, and the lowest found between 0.01 M $CaCl_2$ and 0.05 M $CaCl_2$. For most soil extractants there was a positive relationship between the concentration of Cd extracted from the soil and the concentration of Cd in the plant (Table 6.5). The correlation levels between plant Cd concentration and extractable soil Cd however varied depending upon the plant species and the extractant used. For example extractable NH_4OAc explained 82 % of the variation in maize Cd concentration, however only 56 % for carrot top (Fig 6.1). Likewise, extractable 0.05 M $CaCl_2$ explained 80 % of the variation in ryegrass Cd concentration however only 34 % in clover (Fig 6.2). Similarly 0.01 M $CaCl_2$ could predict 90% of the Cd concentration in carrot root, but could only account for 36 % in lucerne (Fig 6.3). When all plants species were analysed together, extractable 0.05 M $Ca(NO_3)_2$ was the best predictor of plant Cd concentration, although the regression coefficient value was low ($r = 0.44$, $p < 0.0001$) when compared to individual extractants and plant species. A similar result was found by He and Singh (1993a) where several soil extractants were tested as predictors of Cd concentration in oat grain, mixed grass, timothy and ryegrass. When all plant data were analysed together, often correlation coefficients were significantly lower than when individual plant species were analysed. It appears that the Cd removed from the soil by a given extractant may not completely explain the variations in the Cd concentration of plant

Table 6.4 Correlation matrix (r) between soil Cd extracted by different extractants

	0.01 M $CaCl_2$	1 M NH_4NO_3	0.05 M $Ca(NO_3)_2$	1 M NH_4OAc	0.05 M $CaCl_2$	1 M NH_4Cl	0.04 M EDTA	0.05 M AAAc-EDTA
0.01 M $CaCl_2$	1							
1 M NH_4NO_3	0.993	1						
0.05 M $Ca(NO_3)_2$	0.965	0.971	1					
1 M NH_4OAc	0.877	0.907	0.968	1				
0.05 M $CaCl_2$	0.875	0.890	0.970	0.990	1			
1 M NH_4Cl	0.957	0.990	0.960	0.890	0.883	1		
0.04 M EDTA	0.913	0.905	0.958	0.994	0.980	0.898	1	
0.05 M AAAc-EDTA	0.982	0.952	0.949	0.955	0.926	0.947	0.970	1

* $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$, n.s not significant

Table 6.5 Linear correlation coefficients (r) between concentration of Cd extracted from 10 different soils and Cd concentration in selected plant species

Extractants	Cereal			Vegetable				Pasture		
	Maize	*Barley*	*Wheat*	*Cabbage*	*Carrot tops*	*Carrot roots*	*Lettuce*	*Ryegrass*	*Clover*	*Lucerne*
0.05 M $Ca(NO_3)_2$	0.893 ***	0.862 **	0.838 **	0.715 *	0.853 **	0.921 ***	0.802 **	0.884 ***	0.663 *	0.725 *
1 M NH_4NO_3	0.773 **	0.896 ***	0.722 *	0.846 **	0.861 **	0.941 ***	0.683 *	0.863 **	0.757 **	0.637 *
0.01 M $CaCl_2$	0.768 **	0.885 **	0.753 *	0.833 **	0.884 ***	0.950 ***	0.660 *	0.823 **	0.753 *	0.602 n.s
0.05 M $CaCl_2$	0.938 ***	0.795 **	0.883 ***	0.584 n.s	0.775 **	0.843 **	0.899 ***	0.893 ***	0.580 n.s	0.789 **
1 M NH_4OAc	0.908 ***	0.785 **	0.844 **	0.627 n.s	0.746 *	0.837 **	0.868 **	0.894 ***	0.544 n.s	0.780 **
1 M NH_4Cl	0.744 *	0.888 ***	0.690 *	0.850 **	0.905 ***	0.957 ***	0.669 *	0.864 **	0.758 *	0.588 n.s
0.04 M EDTA	0.875 ***	0.788 **	0.811 **	0.661 *	0770 **	0.853 **	0.860 **	0.909 ***	0.550 n.s	0.754 *
0.05 M AAAc-EDTA	0.769 **	0.813 **	0.691 *	0.814 **	0.805 **	0.902 ***	0.767 **	0.886 ***	0.616 n.s	0.665 *

* $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$, n.s not significant

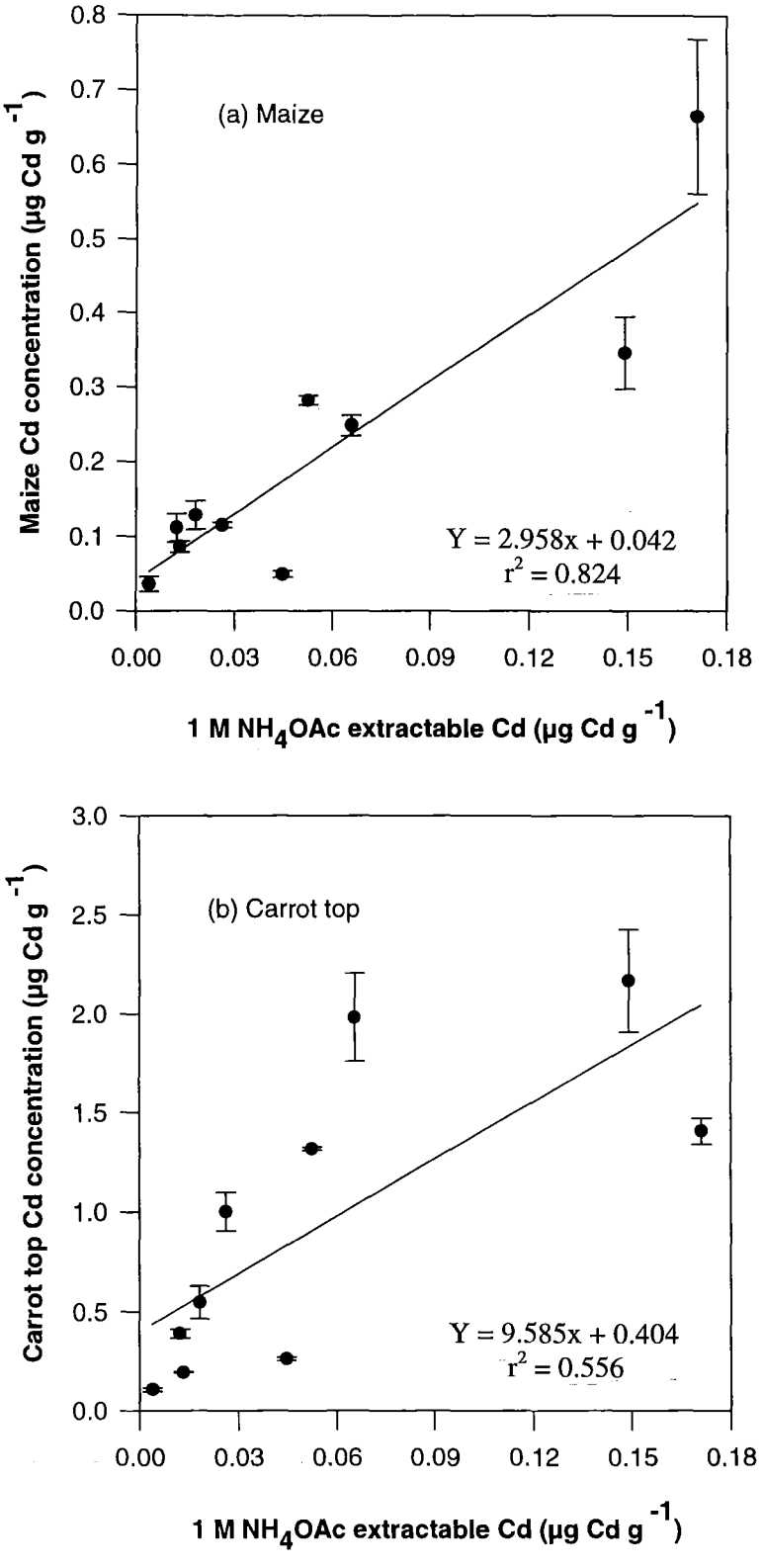


Fig. 6.1 Relationship between 1 M NH_4OAc-extractable Cd and mean Cd concentration in (a) maize and (b) carrot top. Vertical bars denote standard errors of the mean.

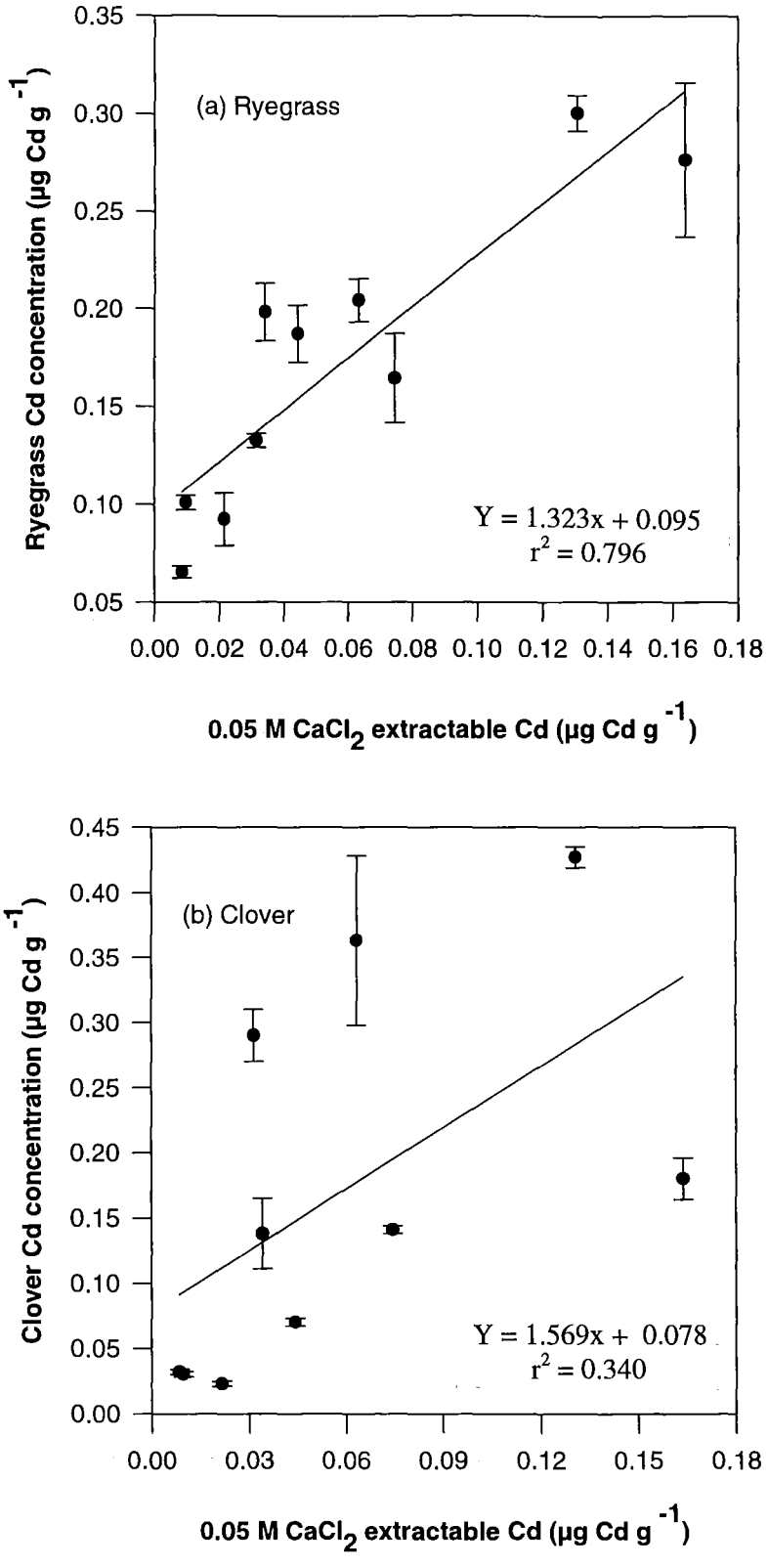


Fig. 6.2 Relationship between 0.05 M $CaCl_2$-extractable Cd and mean Cd concentration in (a) ryegrass and (b) clover. Vertical bars denote standard errors of the mean.

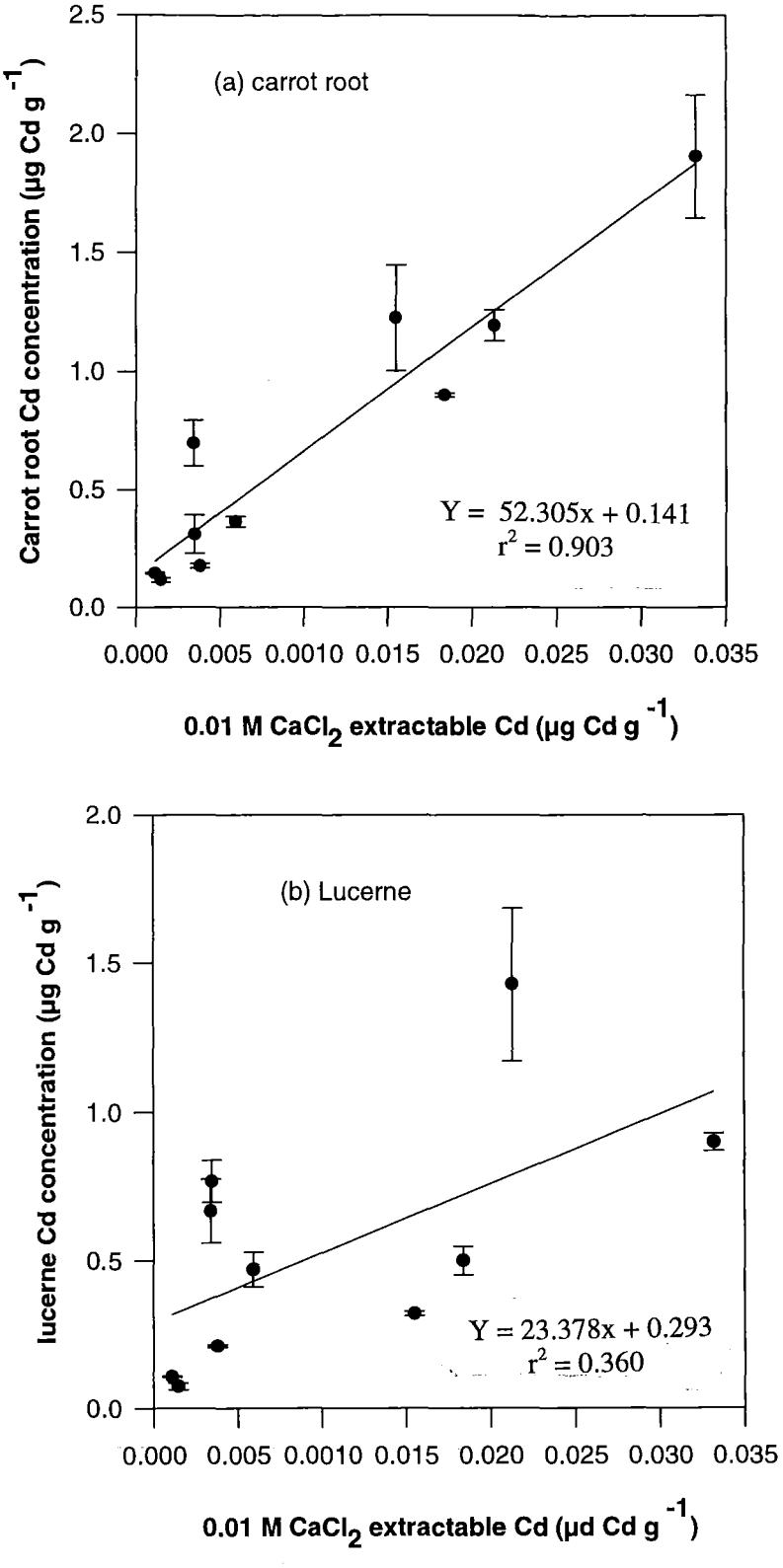


Fig. 6.3 Relationship between 0.01 M $CaCl_2$-extractable Cd and mean Cd concentration in (a) carrot root and (b) lucerne. Vertical bars denote standard errors of the mean.

species when combining different plant species together. Since different plant species vary greatly in their ability to absorb Cd from soils (as will be discussed in the next section) the weak relationship was perhaps not surprising.

There was no relationship found between plant dry weight (g pot^{-1}) and Cd uptake (μg pot^{-1}) ($r = 0.152$) in the different species studied. This indicates that differences in Cd uptake between the plant species were not a function of differences in relative growth rates of the plants. Dry matter weight per pot for each plant species and soil type are given in Asppendix 6.1.

The usefulness of a given extractant to predict plant uptake of Cd will depend on whether the extractant reflects concentrations of Cd in soil solution and the fraction of soil Cd in direct equilibrium with soil solution. Chelating agents such as EDTA have been used widely to predict of Cd phytoavailability. However, Mann and Ritchie (1993) found that EDTA not only extracts Cd from soluble and exchangeable soil sites, but also Cd from strongly bound oxide sites. These authors have suggested EDTA may be more indicative of the total Cd pool in soils rather than plant available forms. Likewise Ure *et al.* (1993) indicate that EDTA can extract Cd from oxide sites, as well as organically and carbonate bound Cd. In other studies with copper (Cu), McLaren and Crawford (1973a) commented that EDTA extracts Cu predominantly from the organic fraction of soil, and Hogg *et al.* (1993) indicated that EDTA overestimates the amount of plant available Cu in soils. DTPA is also widely used as an extractant to predict plant Cd concentrations, and was initially developed for use on calcareous soils, but has often been used on acid soils. He and Singh (1993b) indicate that DTPA may remove non-exchangeable Cd from soils, if consideration of 1 M $MgCl_2$-extractable Cd being exchangeable is valid. Mullins and Sommers (1986) also reported that DTPA extractable Cd was consistently higher than the isotopically exchangeable Cd. Hooda *et al.* (1997) argue EDTA and DTPA are good extractants to predict metal phytoavailability because of their greater strength compared to dilute salt reagents, as they are likely to be sensitive to reduced metal solubilities at higher soil pH or for soils low in metal content.

Other studies have shown that neutral salts, such as $CaCl_2$ or NH_4NO_3 provide the most useful indices of Cd phytoavailability (Haeni and Gupta 1983; Morgan and Alloway 1984; Delshen and Werner 1989). Cadmium extracted by these dilute extractants was more likely to represent phytoavailable concentrations of Cd in equilibrium with the solid phase. These extractants mimic soil solution conditions, such as soil pH and ionic conditions are likely to extract a phytoavailable pool (i.e soluble and exchangeable Cd) and are therefore likely to be powerful predictors of plant Cd uptake. A number of studies have found neutral 1 M NH_4OAc to be successful in predicting Cd uptake in a range plant species. For example John (1972) reported a significant relationship for radish and lettuce, as did Haghiri (1974) for oats. Andersson and Nilsson (1974) also found neutral NH_4OAc was useful to predict plant uptake of Cd in fodder rape. Symeonides and McRae (1977) found significant relationships between radish Cd concentration and a number of extractants including NH_4OAc. Calcium chloride has been used to predict Cd concentrations in both field trials involving clover (Whitten and Ritchie 1991), and in pot trials using lettuce (Andrewes *et al.* 1996). Delshen and Werner (1989) found a linear relationship between 0.1 M $CaCl_2$ extractable Cd concentration in soils and Cd concentration in wheat grain. Krishnamurti *et al.* (1995b) on the other hand found 1 M NH_4Cl to be a very good indicator of the Cd concentration in durum wheat. Calcium nitrate has also been used very successfully to predict Cd uptake in sudax (*Sorghum bicolor* L.) from sludge amended soils (Jing and Logan 1992). These authors consider $Ca(NO_3)_2$ extracts from exchangeable labile fraction of sludge, with the (NO_3^-) ligand forming weak complexes with Cd. Mench *et al.* (1997) also found Cd extracted by 0.1 M $Ca(NO_3)_2$ to be significantly correlated with Cd in maize shoots, and state that an unbuffered salt solution such as $Ca(NO_3)_2$ represents a soluble and exchangeable fraction of soil Cd.

From an analytical viewpoint, an extractant which has low background interference i.e. does not extract a large amount of organic matter, but extracts a sufficient quantity of Cd to be within the working range of a GFAAS is desirable, especially in unpolluted soils. Based on this rationale and the findings in the present study, an unbuffered or neutral extractant such as NH_4OAc, $CaCl_2$ or $Ca(NO_3)_2$ may be regarded as a suitable predictor of plant Cd uptake in unpolluted soils.

6.3.3 Plant Cd concentrations

Different plant species have been shown in a number of studies to vary greatly in their ability to absorb Cd from soils because of genetic differences (MacLean 1976; Hamon *et al.* 1997a). In general, when grown in the same soil, Cd accumulation by different plant species has been shown to decrease in the order, leafy vegetables > root vegetables > grain crops (Bingham 1979; Page *et al.* 1987). For example Hooda *et al.* (1997) found Cd uptake on sludge amended soils decreased in the order spinach >> carrot roots > wheat. The dry matter Cd concentrations for all plant species across the 10 soils, and their associated plant metal transfer ratios (ratio of the concentration of Cd in plant to its concentration in the soil) for the present study are given in Table 6.6. These results show that Cd concentrations across the 10 plant species decreased in the order: Lettuce >> carrot top > carrot root > lucerne > cabbage > wheat 2 = wheat 1 = maize > ryegrass = ryegrass 2 > clover > clover 2 > barley > barley 2. Where (1, 2) refer to the first or second harvest of that particular plant species.

In the majority of cases, the lowest values for Cd concentrations were found for plant species grown on the Summit soil and the highest values observed on the Te Kuiti and Whakatane soils (Table 6.6). The plant species studied accumulated a wide range of Cd concentrations (Fig 6.4). Lettuce accumulated by far the highest concentration of Cd, and is a crop known to have a high capacity to absorb and translocate Cd from the soil to plant tissue (Smilde *et al.* 1992; Del Castilho and Chardon 1995; Brown *et al.* 1996).

The carrot crop, both tops and roots, also accumulated relatively high concentrations of Cd. Interestingly, carrot tops contained significantly higher Cd concentrations than their roots. This observation has also been reported by MacLean (1976); Singh and Nayyar (1990) and Guttormsen *et al.* (1995). He and Singh (1994) reported that vegetative parts of all plant species studied, including carrots, contained higher Cd than their seeds or roots. This phenomenon for carrots has also been shown for lettuce, tobacco and potatoes by MacLean (1976); for radish by Chang *et al.* (1987), for raddish and turnips Singh and Nayyar (1990), and for carrots and turnips by De Pieri *et al.* (1997). This confirms the theory that Cd is a very mobile ion, and can be readily translocated to aerial parts of plants once absorbed by plant roots.

Table 6.6 Mean concentrations of Cd (μg g^{-1} DW), standard error of the mean and associated soil-to-plant transfer coeffecients for all plant species

	Soil 1		Soil 2		Soil 3		Soil 4		Soil 5		Soil 6		Soil 7		Soil 8		Soil 9		Soil 10		Transfer
Species	mean	s.e.	mean	s.e.	mean	s.e.	mean	s.e.	mean	s.e.	mean	s.e.	mean	s.e.	mean	s.e.	mean	s.e.	mean	s.e.	ratio
Maize	**0.281**	0.004	**0.346**	0.031	**0.663**	0.068	**0.248**	0.011	**0.128**	0.012	**0.111**	0.006	**0.036**	0.002	**0.086**	0.006	**0.048**	0.004	**0.115**	0.003	*0.577*
Barley 1	**0.135**	0.020	**0.174**	0.003	**0.121**	0.003	**0.066**	0.001	**0.059**	0.002	**0.034**	0.002	**0.017**	0.003	**0.025**	0.002	**0.050**	0.001	**0.095**	0.005	*0.219*
Barley 2	**0.101**	0.001	**0.097**	0.023	**0.087**	0.004	**0.050**	0.006	**0.063**	0001	**0.037**	0.003	**0.025**	0.001	**0.025**	0.004	**0.028**	0.004	**0.038**	0.004	*0.149*
Wheat 1	**0.339**	0.033	**0.303**	0.022	**0.586**	0.030	**0.186**	0.005	**0.167**	0.001	**0.111**	0.008	**0.030**	0.001	**0.099**	0.002	**0.073**	0.004	**0.021**	0.002	*0.535*
Wheat 2	**0.309**	0.016	**0.289**	0.013	**0.720**	0.104	**0.184**	0.059	**0.116**	0.022	**0.167**	0.015	**0.018**	0.002	**0.080**	0.010	**0.096**	0.008	**0.022**	0.013	*0.622*
Lettuce	**1.008**	0.124	**2.806**	0.194	**4.495**	0.371	**2.215**	0.216	**1.945**	0.022	**1.423**	0.162	**0.273**	0.069	**0.471**	0.052	**1.158**	0.194	**1.775**	0.224	*4.921*
Cabbage	**0.289**	0.001	**1.250**	0.045	**0.200**	0.005	**0.345**	0.042	**0.196**	0.027	**0.072**	0.003	**0.065**	0.008	**0.094**	0.006	**0.040**	0.040	**0.202**	0.018	*0.770*
Carrot top	**1.316**	0.008	**2.166**	0.166	**1.981**	0.145	**1.407**	0.039	**0.549**	0.053	**0.391**	0.027	**0.105**	0.008	**0.195**	0.004	**0.856**	0.011	**1.011**	0.062	*2.796*
Carrot root	**0.900**	0.076	**1.906**	0.175	**1.193**	0.061	**1.224**	0.137	**0.310**	0.014	**0.362**	0.023	**0.116**	0.007	**0.147**	0.004	**0.177**	0.005	**0.697**	0.043	*1.970*
Clover 1	**0.363**	0.065	**0.427**	0.008	**0.184**	0.016	**0.141**	0.003	**0.290**	0.020	**0.023**	0.002	**0.032**	0.002	**0.030**	0.002	**0.070**	0.003	**0.138**	0.027	*0.473*
Clover 2	**0.150**	0.005	**0.411**	0.042	**0.136**	0.017	**0.099**	0.004	**0.138**	0.006	**0.025**	0.002	**0.016**	0.002	**0.045**	0.005	**0.069**	0.004	**0.047**	0.001	*0.319*
Ryegrass 1	**0.204**	0.011	**0.300**	0.009	**2.76**	0.034	**0.164**	0.023	**0.133**	0.004	**0.093**	0.013	**0.066**	0.003	**0.101**	0.004	**0.187**	0.015	**0.198**	0.015	*0.485*
Ryegrass 2	**0.114**	0.006	**0.311**	0.018	**0.135**	0.005	**0.168**	0.011	**0.108**	0.013	**0.034**	0.002	**0.061**	0.008	**0.03**	0.018	**0.031**	0.002	**0.126**	0.007	*0.316*
Lucerne	**0.500**	0.048	**0.900**	0.030	**1.428**	0.258	**0.320**	0.007	**0.768**	0.071	**0.470**	0.059	**0.074**	0.012	**0.107**	0.001	**0.211**	0.004	**0.667**	0.108	*1.529*

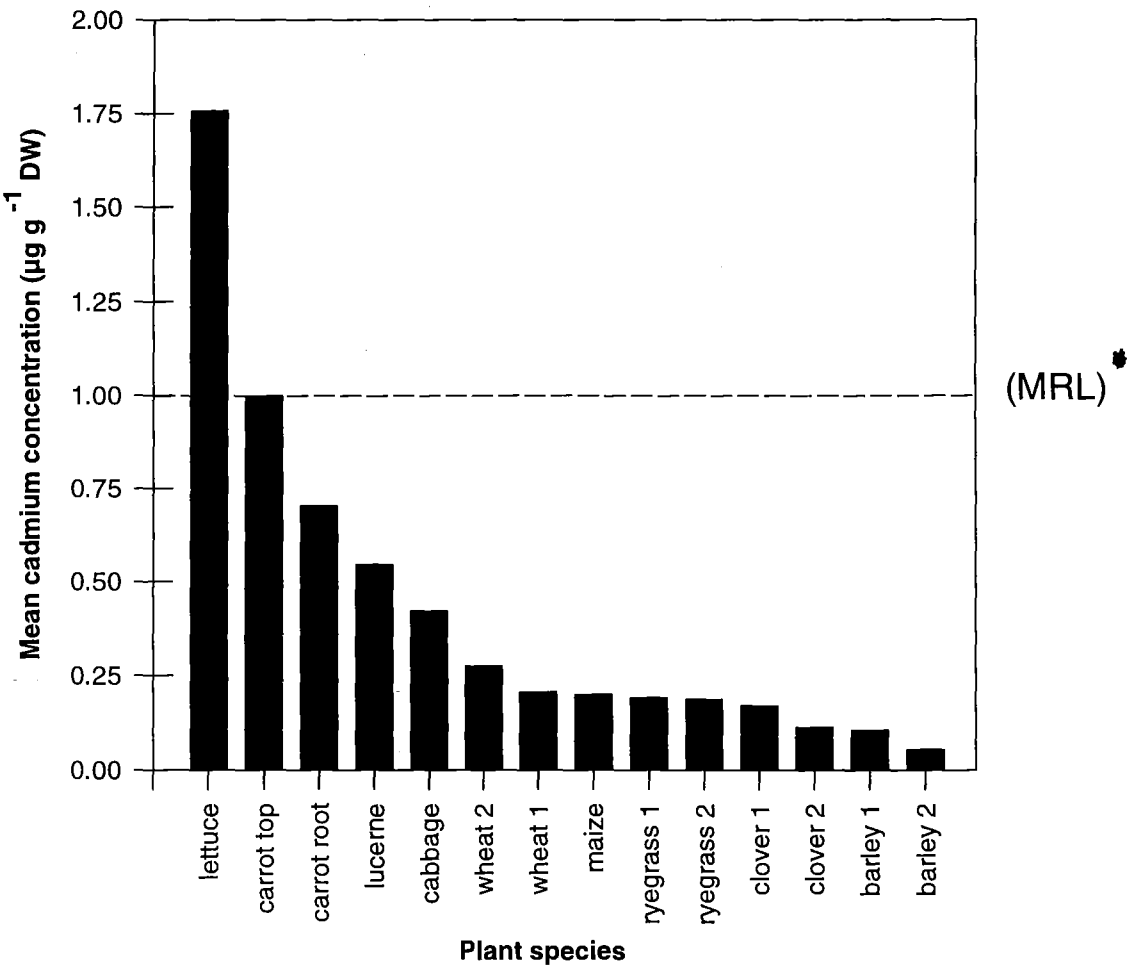


Fig. 6.4 Mean Cd concentration (µg g^{-1} DW) for the different plant species across all ten soils.

* Maximum Residue Level (MRL) is on a fresh weight basis

In contrast, the lowest Cd concentrations were found in two of the pasture species, clover and ryegrass and in the barley crop. Monocotyledonous species such as ryegrass and barley tend to absorb lower quantities of Cd (Bingham *et al.* 1975), and the results in the present study appear to support these previous findings.

The second harvest of ryegrass, clover and barley contained lower Cd concentrations than in the first harvest, with wheat indicating a slight increase. A decrease in Cd uptake with successive harvests for a variety of crops has been reported by several other workers (Mortvedt *et al.* 1981; Bidwell and Dowdy 1987; He and Singh 1994). Guttormsen (1990) showed that Cd concentration in cabbage and carrots were highest in the first harvest as did Singh (1990) for oats and rape. This could be related to a reduction in the available pool of Cd due to fixation and/or Cd removal by the previous crop (He and Singh 1994). Sauerbeck and Styperek (1985) reported evidence of this by showing that a decrease in the Cd concentration in ryegrass during a 3 year period, was mirrored by a decrease in the proportion of $CaCl_2$ extractable Cd. These authors concluded that this was function of binding of Cd by the soil rendering it unavailable.

The New Zealand Department of Health curently has a maximum residue level (MRL) of 1 $\mu g\ g^{-1}$ Fresh Weight (FW) for the Cd content of all foodstuffs for human consumption (except some seafood). Results in this study, although presented in dry weight values, indicate that all crops examined fell below this value (Fig 6.4). There is evidence to indicate that the response of plants to toxic metals such as Cd in pot experiments may greatly exceed uptake under field conditions (De Vries and Tiller 1978). De Vries and Tiller (1978) compared Cd uptake by onions and lettuce grown on sludge amended soils under glasshouse and field environments. Results indicated that lettuce uptake was up to approximately seven fold higher in the glasshouse experiment compared to the field site.

Why was there such a large range in the ability of different plant species to absorb Cd from soil? Hamon *et al.* (1997) recently showed in a study of Cd and Zn uptake in several plant species that canola was unable to access a pool of soil Cd that was available for uptake by other plant species. It was found that all species except canola were accessing a non-

isotopically exchangeable pool of Cd. The mechanisms responsible for this variation in plant uptake are at this stage not fully understood. It is possible that release of organic exudates by the plant roots may modify the flow and availability of plant nutrients and toxic metals such as Cd by acidification, chealation and precipitation reactions in the rhizosphere (Marschner *et al.* 1986; Mench and Martin 1991). This may make it possible for the release of Cd into soil solution from non-exchangeable sites such as carbonate, organic and oxide bound Cd in soils. Cakmak *et al.* (1994) for example showed that during conditions of Fe and Zn deficiency, some monocotyledon species can release root exudates which enhance uptake of these metals by plants. Therefore it may be that leafy plants species such as lettuce are accessing a pool of non-exchangeable Cd in soils, that species such as ryegrass and clover are unable to access.

6.3.4 Soil factors affecting plant Cd concentrations

Contrary to what has been shown in some studies, (e.g. He and Singh 1993b) there were no signficant relationships between some common soil properties such as CEC, pH, soil texture, soil K_d values, and plant Cd concentrations. There were however strong positive relationships between cumulative native Cd desorption, total soil Cd, amorphous Al oxides, Mn oxides, total soil P and plant Cd concentrations. The relationships between plant Cd concentrations and these soil parameters probably reflect a positive relationship with total Cd (Table 6.7).

Table 6.7 Coefficients of correlation (r) between total Cd and soil properties

	Native Cd desorbed	Total P	Org. C	Mn	Amor Al
Total Cd	0.94***	0.93***	0.83**	0.77**	0.77**

* $p < 0.05$; ** $p < 0.01$; *** $p < 0.001$; n.s., not significant

Total soil Cd was significantly correlated with plant Cd for all species except lucerne (Table 6.8). Past research has demonstrated a positive correlation between total Cd applied to soil and the plant uptake of Cd (Chumbley and Unwin 1982; Jackson and Alloway 1991; Sloan *et al.* 1997; Loganathan *et al.* 1997). Lund *et al.* (1981) for example showed that Cd concentrations in three crops increased as the Cd concentrations in the soils increased. Hooda *et al.* (1997) identified total soil Cd as the most important soil variable controlling

Cd concentrations in carrots, spinach, and wheat. However pH, and clay content also played a regulating role in the plant availability of Cd. Like the present study, Hooda *et al.* (1997) found the effects of CEC, organic carbon, free Fe oxides and Mn oxides on metal accumulation were less clear. Likewise, Jinadasa *et al.* (1997) found in a survey of Cd concentrations in vegetable crops that Cd concentrations were generally poorly correlated with soil properties.

It appears that the sorption and desorption capacity of the soils studied, expressed in terms of clay %, pH, CEC and soil K_d values were not as important as total soil Cd concentrations in controlling plant Cd concentration. Poor correlations between soil properties and plant Cd concentrations may have been due to the small number of soils used for statistcal comparisons.

Table 6.8 Coefficients of correlation (*r*) between total Cd and plant species

Plant species	Total Cd
maize	0.697*
barley	0.829**
wheat	0.622*
cabbage	0.902***
carrot top	0.812**
carrot root	0.914***
lettuce	0.689**
ryegrass	0.841**
clover	0.697*
lucerne	0.619n.s

* $p < 0.05$; ** $p < 0.01$; *** $p < 0.001$; n.s., not significant

6.4 Conclusions

The suitability of eight common soil extractants to predict plant uptake of Cd from several New Zealand soils at low Cd concentrations was investigated. In addition, a study of Cd uptake by several vegetable, cereal and pasture crops in relation to different soil types was undertaken. The concentration of Cd extracted varied with each extractant, 0.05 M AAAc-EDTA extracted the greatest concentration whereas 0.01 M $CaCl_2$ the least. Results indicate that for all extractants tested, there was a direct relationship between the concentration of Cd extracted and the concentration of Cd in plant material, however this depended upon the plant species and individual soil extractant. When all plants were

analysed together, it was found that 0.05 M $Ca(NO_3)_2$ was the best predictor of plant Cd concentration. Plant Cd concentration varied greatly between different plant species, greatest uptake was found in lettuce and to a lesser extent carrot tops, and least in ryegrass, clover and barley. All plants were within the MRL for the Cd content of all foodstuffs intended for human consumption. Total Cd concentration was found to be the most important soil parameter influencing plant Cd concentrations.

Chapter 7

Effect of soil pH on Cadmium phytoavailability in some New Zealand soils

7.1 Introduction

Cadmium phytoavailability has been shown to be influenced by a wide range of soil and plant variables. Soil pH is often regarded as the major variable controlling Cd uptake from soils (Chaney and Hornick 1978). A number of studies have shown that with increasing soil pH, there is a corresponding decrease in plant Cd concentration (e.g. Guttormsen *et al.* 1995; Han and Lee 1996). In contrast, however there have been several field trials in which liming to increase soil pH has resulted in no change in plant Cd concentration (Jaakola 1977; Hemphill *et al.* 1982; Sparrow *et al.* 1993; Li *et al.* 1996), and has in some cases liming increased plant Cd concentration (Sparrow *et al.* 1993; Maier *et al.* 1997).

Results of experiments carried out in Chapters 4 and 5 have identified soil pH as an important soil property controlling sorption/desorption and solubility of native and added soil Cd, and therefore likely to play a role in influencing Cd phytoavailability. As a soil property that is relatively easy to manipulate, soil pH may be a powerful tool in the management of plant Cd concentrations. The objectives of this study was to evaluate the effect of soil pH on plant Cd concentration at low soil Cd concentrations. As already discussed there is a dearth of relevant studies using Cd concentrations relevant to New Zealand soils. In addition, the suitability of 8 soil extractants which were investigated in Chapter 6 to predict Cd concentrations in different plant species were re-evaluated in this study.

7.2 Materials and methods

7.2.1 Soil sampling and analysis

Three topsoil samples (Patumahoe, Te Kuiti and Tai Tapu soils) Table 7.1, were selected to determine the effect of soil pH on plant Cd concentrations. The samples were ground moist to pass through a 4 mm stainless steel sieve, and a subsample taken. The subsamples were air-dried and ground to pass through a 2 mm stainless steel sieve prior to laboratory

analysis. Soil pH was measured in a water suspension using a soil:solution ratio of 1:2.5. Soil texture was determined by the pipette method described by Day (1965). Total carbon content in the soils was determined by LECO CNS 2000 analyser. Total Cd was determined by a nitric acid microwave digestion method (USEPA SW 846-3051). Cation exchange capacity (CEC) was determined by ammonium acetate leaching at pH 7.0 (Blakemore *et al.* 1987). Amorphous iron (Fe) and aluminium (Al) oxides were determined by ammonium oxalate extraction (Blakemore *et al.* 1987). Crystalline Fe and Al oxides were determined by the oxalate/ascorbic acid extraction method of Shuman (1982), correcting the results for amorphous Fe and Al. Manganese oxide content was determined by extraction with 0.1 M hydroxyl-amine hydrochloride (Shuman 1982). Bioavailable P (Olsen P) was determined by bicarbonate extraction and total P was determined by NaOH fusion (Blakemore *et al.* 1987).

7.2.2 Pot trial

The three desired soil pH values (pH 5.5, 6.0, 7.0) were achieved from addition of either CaOH or HCl to the original soils, and soils left to equilibrate for 4 weeks before the beginning of the pot trial. Approximately 2kg of field moist < 4 mm sieved soil was weighed into plastic pots lined with perforated polythene plastic bags. A basal nutrient solution containing NH_4NO_3, $CaH_4(PO_4)_2.H_2O$, K_2HPO_4, K_2SO_4, $MgSO_4.H_2O$ which supplied the equivalent of 100, 40, 60, 17, 10 kg^{-1} ha^{-1} of N, P, K, S and Mg respectively was applied (25 mL pot^{-1}), to each pot at the start of the trial, with a second application after three weeks. All fertiliser applied was analytical grade (AR). Soils were made up to 75 % field capacity moisture content and these weights were maintained throughout trial by the addition of deionised water. Five different plant species were planted and grown: wheat (*Triticum aestivum* L.), white clover (*Trifolium repens* L.), lettuce (*Lactuca sativa L.*), carrot (*Daucus carota* L.), and ryegrass (*Lolium perenne* L.). Eight wheat seeds were sown into each pot, and two weeks after germination, thinned to six plants. Carrot was oversown at 0.4 g per pot and thinned to approximately 15 plants per pot. Lettuce was oversown at 10 seeds per pot and thinned to four per pot after 2 weeks. Pasture species were sown on weight basis, at 0.4 g per pot. The tops of the pots were initially covered until germination of the seeds had taken place. Each crop was replicated in triplicate, and the pots arranged in a randomised complete block design in a glasshouse. Above ground

Table 7.1 Properties of the soils used for the pot trial

Soil type	pH	sand	silt	clay	Org. C	Total P	Olsen P	CEC	Mn	Fe		Al		Total Cd
										crystal	amorp	crystal	amorp	
		(%)					($\mu g\ g^{-1}$)	($cmol_c\ kg^{-1}$)	($\mu g\ g^{-1}$)	(%)				($\mu g\ Cd\ g^{-1}$)
Patumahoe	5.4	22.5	71.2	6.3	7.4	0.171	17	10.8	170.0	0.88	0.68	0.68	2.30	0.78
Te Kuiti	4.9	24.9	45.3	29.8	13.0	0.291	13	9.2	620.0	0.19	0.80	0.32	3.10	1.34
Tai Tapu	5.5	27.9	32.8	39.3	3.6	0.103	45	11.1	56.5	0.77	0.28	0.27	0.16	0.19

parts of each plant were analysed for Cd content. This included wheat straw and wheat grain being analysed seperately, as was carrot top and carrot root. Ryegrass was harvested 3 times throughout the trial.

7.2.3 Plant analysis

Plants were harvested 10 mm above soil height with stainless steel scissors, shredded and dried at 65 °C. The dried sample was finely ground using a stainless steel roller. Subsamples of ground plant material (0.5 g) were digested in 10 mL 69% Aristar grade nitric acid and heated on a digestion block up to 140 °C over a period of 7 h. The digest was then made up to 20 mL with deionised water and filtered through a Whatman No. 42 paper filter paper. Duplicate analysis of all the plant samples was made together with reagent blanks. Cadmium was determined in the extracts by graphite furnace atomic absorption spectrophotometry (GFAAS) with a deuterium background correction and phosphoric acid (H_3PO_4) was used as a modifier.

7.2.4 Soil extractions

Eight different extractants were selected to assess Cd phytoavailability (Table 7.2). The extraction procedure (i.e. extraction time and soil:solution ratios) were the same as those recommended by the referenced investigators (Table 7.2). In order to eliminate potential matrix effects of salts in the extracting solutions during analysis, Cd standards were prepared in the respective salt solution using analytical grade chemicals. Cadmium was determined in the extracts by graphite furnace atomic absorption spectrophotometry (GFAAS) with a deuterium background correction. All analyses were carried out in triplicate, and data presented as the mean values of the triplicate determinations.

7.2.5 Statistical methods

To normalise data and to achieve homogeneity of variance, all data were log transformed. Analysis of variance (ANOVA) was carried out using SYSTAT statistical package and linear regression analysis using Minitab version 9.2.

Table 7.2 Methods of assessing phytoavailable Cd in soil

Extractant	Reference	Soil/solution ratio	Time of extraction (h)
0.05 M $Ca(NO_3)_2$	Jing and Logan (1992)	1:10	16 h
1 M NH_4NO_3	Symeonides and McRae (1977)	1:10	1 h
0.01 M $CaCl_2$	Whitten and Ritchie (1991)	1:5	16 h
0.05 M $CaCl_2$	Novozamsky *et al.* (1993)	1:10	0.3 h
1 M NH_4OAc	Symeonides and McRae (1977)	1:10	1 h
1 M NH_4Cl	Krishnamurti *et al.* (1995b)	1:6	16 h
0.04 M EDTA	McLaren *et al.* (1984)	1:4	2 h
0.05 M AAAc-EDTA	Lakanen and Ervio (1971)	1:10	1 h

7.3 Results and discussion

7.3.1 Plant Cd concentrations

For the purposes of the main analysis, plant Cd concentrations in wheat straw and grain were analysed together as were carrot top and carrot root and all three ryegrass harvests. Total wheat concentration (i.e. wheat straw and grain) was calculated by multipling wheat straw concentration by its dry matter weight and adding this to wheat grain concentration multiplied by its dry matter weight, and then dividing the sum by the combined straw and grain dry weights. The same procedure was undertaken for carrot and ryegrass. The main effects and interactions between soil type, pH and plant species on plant Cd concentrations are presented in Table 7.3.

It indicates that there were significant differences in plant Cd concentrations across the three soils studied, with greatest Cd uptake from the Patumahoe soil and the least from the Tai Tapu soil, even though the Te Kuiti soil had the highest total Cd concentration (Table 7.1). There were also significant differences in Cd concentrations with respect to soil pH. With increasing pH there was a trend towards decreasing plant Cd concentrations. Plant Cd concentrations generally followed the trends observed in the literature (Bingham 1979; Page *et al.* 1987) and the results which were found in the first pot trial (Chapter 6). Results show that Cd concentrations in the different plant species decreased in the order: lettuce >> wheat > ryegrass > carrot > clover. Cadmium concentrations in lettuce were significantly higher than the other four plants studied.

Table 7.3 Main effect means and significance of interactions of soil type, pH, and plant species on plant Cd concentrations

	$\log_{10}$ (Cd concentration)	Transformed data (Cd concentration) ($\mu g\ Cd\ g^{-1}$)
Soil type		
Patumahoe	-0.22	(0.60)
Te Kuiti	-0.53	(0.30)
Tai Tapu	-0.70	(0.20)
LSD (5%)	0.03	
Soil pH		
5.5	-0.32	(0.48)
6.0	-0.44	(0.36)
7.0	-0.70	(0.20)
LSD (5%)	0.03	
Plant type		
Wheat	-0.59	(0.26)
Clover	-0.66	(0.22)
Lettuce	0.057	(1.15)
Carrot	-0.62	(0.24)
Ryegrass	-0.61	(0.25)
LSD (5%)	0.040	
Significance of interactions		
Soil x pH	***	
Soil x plant	***	
pH x plant	***	
Soil x plant x pH	***	

* $p < 0.05$; ** $p < 0.01$; *** $p < 0.001$; n.s., not significant

Table 7.4 shows the main effects and significant interactions between and soil type, pH and plant species on plant dry matter. Plant dry matter was highest for the Tai Tapu soil and lowest for the Te Kuiti soil. There was no overall consistent pH effect on dry matter production, with an increase between pH 5.5-6.0 and then a decrease in dry matter between 6.0-7.0. This relationship may have been strongly influenced by the decrease in dry matter production between pH 6.0 and 7.0 for the clover species for the Patumahoe and Te Kuiti soils and wheat species for the Te Kuiti soil. With regard to plant species, highest dry matter was recorded for wheat and carrot and lowest for clover (Table 7.4). The effects of pH on dry matter for individual plants and soils are shown in (Fig 7.1).

Table 7.4 Main effect means and significance of interactions of soil type, pH, and plant species on plant dry matter production

	$\log_{10}$ (Cd concentration)	Transformed data (plant dry weight g)
Soil type		
Patumahoe	0.90	(7.88)
Te Kuiti	0.72	(5.30)
Tai Tapu	0.94	(8.71)
LSD (5%)	0.03	
Soil pH		
5.5	0.86	(7.26)
6.0	0.88	(7.58)
7.0	0.82	(6.60)
LSD (5%)	0.03	
Plant type		
Wheat	1.12	(13.10)
Clover	0.53	(3.37)
Lettuce	0.59	(3.93)
Carrot	1.11	(12.83)
Ryegrass	0.92	(8.33)
LSD (5%)	0.04	
Significance of interactions		
Soil x pH	***	
Soil x plant	***	
pH x plant	***	
Soil x plant x pH	***	

* $p < 0.05$; ** $p < 0.01$; *** $p < 0.001$; n.s., not significant

With the exception of the Te Kuiti soil for wheat, there was a significant decrease in plant Cd concentration with an increase in soil pH from 5.5 to 7.0 for all plant species and across all soil types (Fig 7.2). The effect of soil pH on plant Cd concentrations varied considerably between plant species and soil type. For example, for the Patumahoe soil there was a 55% reduction in ryegrass Cd concentration with a pH increase from 5.5 to 7.0, however for the same soil and pH range, there was a 76% decrease in clover Cd concentration. Similarly for the Tai Tapu soil, while there was a only a 39% reduction in wheat Cd concentration, by comparison there was a 78% reduction in Cd concentration for

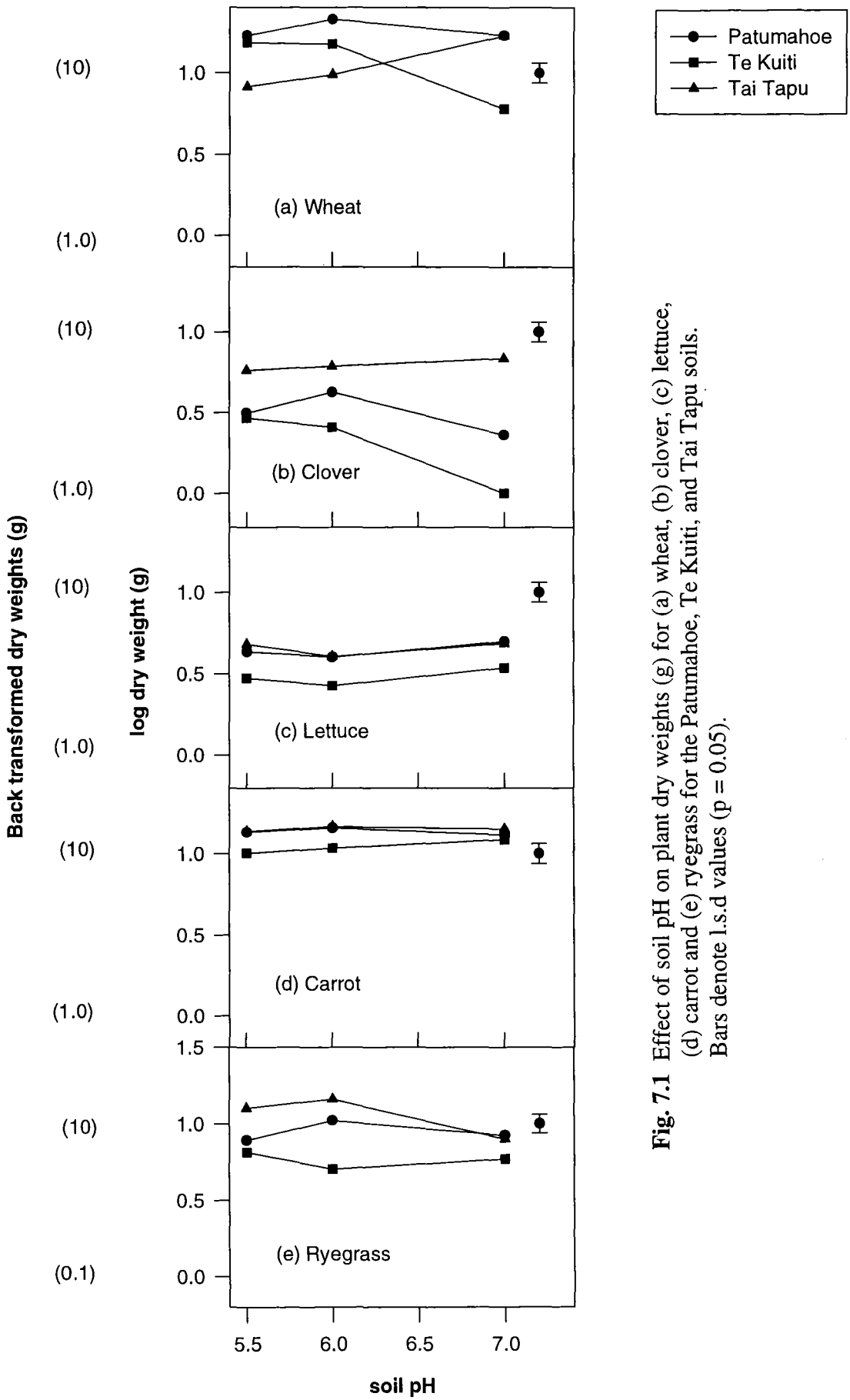


Fig. 7.1 Effect of soil pH on plant dry weights (g) for (a) wheat, (b) clover, (c) lettuce, (d) carrot and (e) ryegrass for the Patumahoe, Te Kuiti, and Tai Tapu soils. Bars denote l.s.d values ($p = 0.05$).

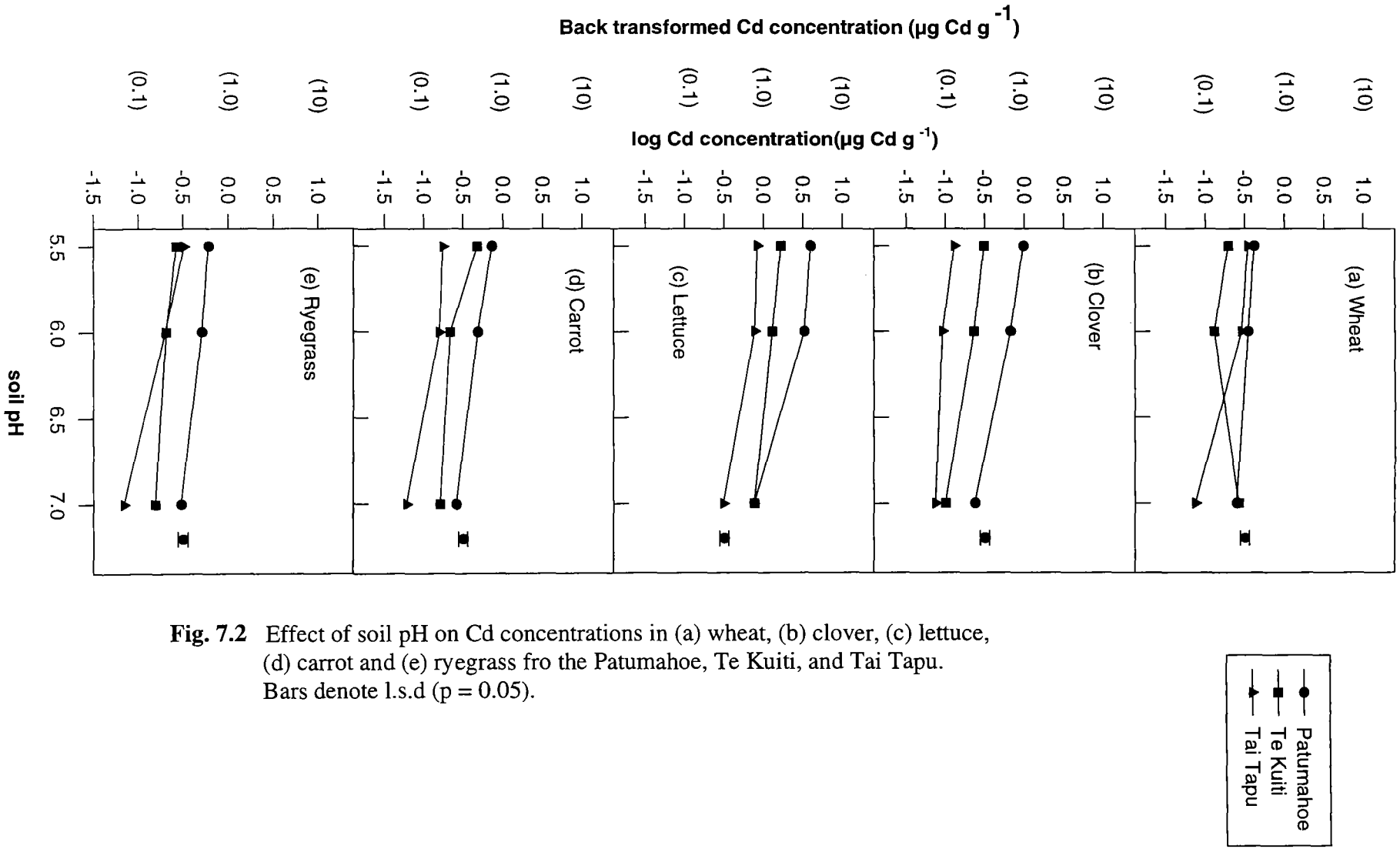


Fig. 7.2 Effect of soil pH on Cd concentrations in (a) wheat, (b) clover, (c) lettuce, (d) carrot and (e) ryegrass fro the Patumahoe, Te Kuiti, and Tai Tapu. Bars denote l.s.d (p = 0.05).

ryegrass over pH 5.5 to 7.0. The decrease in plant Cd concentration as pH increases, was a result of the effect pH has on retention of Cd by soil surfaces. As soil pH increases, sorption of Cd onto soil components, i.e. clay, organic matter and soil oxides also increases. There was also an accompanying decrease in desorption of Cd from these components into soil solution with increasing soil pH (Gray *et al.* 1998). Therefore, increasing soil pH leads to a reduction of Cd in soil solution, the Cd pool in soils most readily available for plant uptake. This was substantiated by the findings in Chapter 5, which highlighted the importance of pH in controlling Cd solubility in soils. There have been a number of studies showing the effect of pH has on plant uptake (John 1972; MacLean 1976; Miller *et al.* 1976; Street *et al.* 1978; Eriksson 1989; Xue and Harrison 1991). Han and Lee (1996) showed Cd uptake in radishes was significantly decreased after liming. While Guttormsen *et al.* (1995), examined the effect of soil pH on Cd uptake by cabbage and carrot over 3 years in a field trial, and at pH 5.5, Cd concentrations in cabbage and carrot were 23 and 46 % higher than at pH 6.5. Whereas Hooda and Alloway (1997) showed that liming soil to pH 7 prior to sowing significantly reduced Cd concentrations in carrots and spinach.

Table 7.5 shows data for Cd concentrations in different plant parts and successive ryegrass harvests. As found and discussed in the Chapter 6, carrot tops again accumulated higher concentrations of Cd than did carrot root. Wheat straw contained higher Cd concentrations than did wheat grain across all three soils. This corresponds with the findings of He and Singh (1994), who found that Cd concentrations were higher in vegetative parts of plants compared to their seeds or roots, and also the findings of Oborn *et al.* (1995), who reported that Cd concentrations in wheat straw were twice as high as Cd concentrations in wheat grain. Although Cd was readily translocated to aerial parts of plants, compared to other heavy metals such as lead, it doesn't appear to be concentrated in the fruiting bodies of plants. There was no significant change in ryegrass Cd concentrations with successive harvests.

Wheat grain Cd concentrations for the Patumahoe soil however, showed no consistent pH effect, with grain concentration increasing and then decreasing with increasing, even though an increase in soil pH reduced Cd content in wheat straw (Table 7.5). Similar findings have also been shown by Smith (1994), where liming sludge-amended soils over a

Table 7.5 Mean cadmium concentrations (μg Cd g^{-1} D.W) in wheat straw and grain, carrot top and root, and three successive ryegrass harvests

		Mean Cd concenectration (μg Cd g^{-1} DW)						
Soil Type	**pH**	**Wheat straw**	**Wheat grain**	**Carrot top**	**Carrot root**	**Ryegrass 1**	**Ryegrass 2**	**Ryegrass 3**
Patumahoe	5.5	0.561	0.104	2.440	1.267	0.518	0.770	0.546
	6.0	0.438	0.196	1.370	0.896	0.580	0.593	0.516
	7.0	0.317	0.123	0.671	0.411	0.413	0.379	0.161
Te Kuiti	5.5	0.235	0.130	0.879	0.787	0.304	0.295	0.214
	6.0	0.161	0.094	0.479	0.330	0.280	0.220	0.110
	7.0	0.313	0.072	0.364	0.215	0.163	0.170	0.137
Tai Tapu	5.5	0.489	0.255	0.693	0.363	0.333	0.311	0.325
	6.0	0.302	0.116	0.430	0.287	0.200	0.190	0.201
	7.0	0.257	0.064	0.185	0.142	0.065	0.079	0.063

pH range 3.9-7.6 substantially reduced Cd concentration in potatoes, ryegrass and oat straw, but had no effect on oat grain. Hooda *et al.* (1997) also found that liming had no significant effect on wheat grain metal contents. Similarly, Oborn *et al.* (1995) showed that the concentrations of Cd in potatoes, carrots and wheat straw were significantly negatively correlated with soil pH however there was no relationship with wheat grain. It appears in some cases e.g. Patumahoe soil, liming may be less likely to control metal accumulations in the grain of wheat, but for the other soils (i.e. Tai Tapu and Te Kuiti) it was successful.

Wheat straw Cd concentrations also showed inconsistent pH effects for the Te Kuiti soil, with a decrease in Cd concentration with an increase in soil pH from 5.5 to 6.0 and then an increase in wheat straw Cd concentration (Table 7.5). Eriksson (1989) found that in many cases ryegrass Cd concentration tended to increase with increased pH, in particular for a clay soil when no Cd was added. He and Singh (1994) also found an increase in Cd concentration in ryegrass and oat grain on a loam soil with an increase in soil pH. One possible explanation for the increase in Cd at higher pH, although not tested, was that with increasing pH there was increased root interception, thereby allowing more opportunity for Cd uptake, although this phenomenon appeared to only effect the wheat crop. Another explanation may be the significant ($p < 0.05$) decrease in dry matter production between pH 6.0 and 7.0 for the Te Kuiti soil, which may have resulted in an increase in Cd

concentration. Plant dry matter production has been shown to effect plant Cd concentrations in other studies (Loganathan *et al.* 1997).

7.3.2 Soil Extractants

Eight chemical extractants were tested as predictors of plant Cd concentrations. The concentrations of Cd extracted varied widely, differing for soil type, soil pH and extractant used. Tables 7.6a - h show the main effects of soil type and pH on the Cd extracted by the different reagents. For seven of the extractants, the greatest concentration of Cd extracted was from the Patumahoe soil, whilst the lowest Cd extracted was from the Te Kuiti soil for six of the extractants. With the exception of AAAc-EDTA, the interaction of soil and pH was significant ($p < 0.001$) in all cases. The mean concentrations of Cd extracted for all soils was in the order: 0.05 M AAAc-EDTA > 0.04 M EDTA > 1 M NH_4Cl > 1 M NH_4OAc > 0.05 M $CaCl_2$ > 0.05 M $Ca(NO_3)_2$ > 1 M NH_4NO_3 > 0.01 M $CaCl_2$. As was found in Chapter 6, the greatest concentrations of Cd extracted were from the buffered, chelate-based reagent AAAc-EDTA and least from 0.01 M $CaCl_2$. For all extractants, excluding 0.05 M AAAc-EDTA and 0.04 M EDTA, there were significant decreases in the concentration of Cd extracted from the soil as pH increased from 5.5 to pH 7.0 (Table 7.7). For AAAc-EDTA there was a significant decrease in Cd extracted for the Tai Tapu soil from pH 5.5 to 6.0, however there were no significant differences in Cd concentrations extracted from the other soil types and pHs. For 0.04 M EDTA, in some cases there was a decrease in the concentration of Cd extracted with increased pH (e.g. Patumahoe soil pH 5.5 - 6.0), while in other cases there was no significant difference (e.g. Tai Tapu soil pH 5.5 - 6.0).

Table 7.8 shows the supernatant pHs for extractants across all soils and pHs. It indicates that $CaCl_2$, NH_4NO_3, $Ca(NO_3)_2$, and NH_4Cl were sensitive to soil pH and in general supernatant pH's were within 0.3 - 0.4 pH units of the soil water pH. This type of relationship for pH and NH_4NO_3 has been previously reported by He and Singh (1994) and Guttormsen *et al.* (1995) and for $CaCl_2$ by (Sauerbeck and Styperek 1985; Jackson and Alloway 1991; Whitten and Ritchie 1991; Andrewes *et al.* 1996). In contrast, buffered extractants were not sensitive to soil pH, with AAAc-EDTA and NH_4OAc reflecting the pH of the original extracting solution (pH 4.65 and pH 7.0 respectively).

Table 7.6a Main effect means and significance of interactions of soil type, pH and 0.01 M $CaCl_2$

	log_{10} (0.01 M $CaCl_2$) (Cd concentration)	**Transformed data (Cd concentration) (µg Cd kg^{-1})**
Soil type		
Patumahoe	0.44	(2.75)
Te Kuiti	0.13	(1.34)
Tai Tapu	0.50	(3.18)
LSD (5%)	0.01	
Soil pH		
5.5	1.02	(10.39)
6.0	0.22	(1.67)
7.0	-0.17	(0.68)
LSD (5%)	0.01	
Significance of interactions		
Soil x pH	***	

* $p < 0.05$; ** $p < 0.01$; *** $p < 0.001$; n.s., not significant

Table 7.6b Main effect means and significance of interactions of soil type, pH and 1 M NH_4NO_3

	log_{10} (1 M NH_4NO_3) (Cd concentration)	**Transformed data (Cd concentration) (µg Cd kg^{-1})**
Soil type		
Patumahoe	0.70	(4.97)
Te Kuiti	0.50	(3.14)
Tai Tapu	0.63	(4.31)
LSD (5%)	0.05	
Soil pH		
5.5	1.11	(12.86)
6.0	0.43	(2.71)
7.0	0.29	(1.92)
LSD (5%)	0.05	
Significance of interactions		
Soil x pH	***	

* $p < 0.05$; ** $p < 0.01$; *** $p < 0.001$; n.s., not significant

Table 7.6c Main effect means and significance of interactions of soil type, pH and 0.05 M $Ca(NO_3)_2$

	log_{10} (0.05 M $Ca(NO_3)_2$ (Cd concentration)	**Transformed data (Cd concentration) (µg Cd kg^{-1})**
Soil type		
Patumahoe	1.22	(16.70)
Te Kuiti	0.83	(6.83)
Tai Tapu	1.00	(9.92)
LSD (5%)	0.05	
Soil pH		
5.5	1.52	(33.31)
6.0	1.03	(10.59)
7.0	0.51	(3.21)
LSD (5%)	0.05	
Significance of interactions		
Soil x pH	***	

* $p < 0.05$; ** $p < 0.01$; *** $p < 0.001$; n.s., not significant

Table 7.6d Main effect means and significance of interactions of soil type, pH and 1 M NH_4OAc

	log_{10} (1 M NH_4OAc) (Cd concentration)	**Transformed data (Cd concentration) (µg Cd kg^{-1})**
Soil type		
Patumahoe	1.73	(53.65)
Te Kuiti	1.55	(35.29)
Tai Tapu	1.58	(38.32)
LSD (5%)	0.009	
Soil pH		
5.5	1.88	(77.22)
6.0	1.64	(44.11)
7.0	1.33	(21.30)
LSD (5%)	0.009	
Significance of interactions		
Soil x pH	***	

* $p < 0.05$; ** $p < 0.01$; *** $p < 0.001$; n.s., not significant

Table 7.6e Main effect means and significance of interactions of soil type, pH and 1 M NH_4Cl

	log_{10} (1 M NH_4Cl) (Cd concentration)	**Transformed data (Cd concentration) (µg Cd kg^{-1})**
Soil type		
Patumahoe	1.95	(89.51)
Te Kuiti	1.74	(55.30)
Tai Tapu	1.80	(63.75)
LSD (5%)	0.02	
Soil pH		
5.5	2.38	(242.00)
6.0	1.85	(70.26)
7.0	1.27	(18.60)
LSD (5%)	0.02	
Significance of interactions		
Soil x pH	***	

* $p < 0.05$; ** $p < 0.01$; *** $p < 0.001$; n.s., not significant

Table 7.6f Main effect means and significance of interactions of soil type, pH and 0.05 M $CaCl_2$

	log_{10} (0.05 M $CaCl_2$) (Cd concentration)	**Transformed data (Cd concentration) (µg Cd kg^{-1})**
Soil type		
Patumahoe	1.39	(24.32)
Te Kuiti	1.04	(11.04)
Tai Tapu	1.26	(18.13)
LSD (5%)	0.03	
Soil pH		
5.5	1.84	(69.50)
6.0	1.27	(18.51)
7.0	0.58	(3.78)
LSD (5%)	0.03	
Significance of interactions		
Soil x pH	***	

* $p < 0.05$; ** $p < 0.01$; *** $p < 0.001$; n.s., not significant

Table 7.6g Main effect means and significance of interactions of soil type, pH and 0.04 M EDTA

	log_{10} (0.04 M EDTA) (Cd concentration)	**Transformed data (Cd concentration) (µg Cd kg^{-1})**
Soil type		
Patumahoe	2.30	(200.87)
Te Kuiti	2.27	(188.05)
Tai Tapu	2.00	(100.31)
LSD (5%)	0.02	
Soil pH		
5.5	2.23	(168.27)
6.0	2.19	(154.44)
7.0	2.16	(145.81)
LSD (5%)	0.02	
Significance of interactions		
Soil x pH	***	

* $p < 0.05$; ** $p < 0.01$; *** $p < 0.001$; n.s., not significant

Table 7.6h Main effect means and significance of interactions of soil type, pH and 0.05 M AAAc-EDTA

	log_{10} (0.05 M AAAc-EDTA) (Cd concentration)	**Transformed data (Cd concentration) (µg Cd kg^{-1})**
Soil type		
Patumahoe	2.67	(463.55)
Te Kuiti	2.80	(634.16)
Tai Tapu	2.15	(142.12)
LSD (5%)	0.05	
Soil pH		
5.5	2.55	(357.44)
6.0	2.54	(344.11)
7.0	2.53	(339.55)
LSD (5%)	0.05	
Significance of interactions		
Soil x pH	n.s	

* $p < 0.05$; ** $p < 0.01$; *** $p < 0.001$; n.s., not significant

Table 7.7 Mean back transformed Cd concentrations (μg Cd kg^{-1}) extracted from pot trial soil by all eight reagents

Soil type	pH	0.01 M $CaCl_2$	1M NH_4NO_3	0.05 M $Ca(NO_3)_2$	1M NH_4OAc	0.05 M $CaCl_2$	1M NH_4Cl	0.04 M EDTA	0.05 M AAAc-EDTA
Patumahoe	5.5	21.10	20.90	58.21	104.7	134.8	360	220	445
	6.0	1.95	2.97	13.80	60.8	27.8	113	191	458
	7.0	0.57	1.98	8.79	24.4	3.9	17	194	493
Te Kuiti	5.5	3.02	5.26	16.90	66.9	35.3	245	209	702
	6.0	1.68	2.35	10.10	33.8	10.3	39	173	595
	7.0	0.49	2.26	1.80	19.4	3.7	17	184	615
Tai Tapu	5.5	17.70	19.40	37.50	65.8	70.6	159	104	163
	6.0	1.40	2.90	8.40	42.0	22.2	77	112	150
	7.0	1.30	1.50	3.00	20.3	3.8	21	87	130
LSR (5%)[A]		1.83	1.22	1.19	1.04	1.13	1.08	1.07	1.20

[A] Least Significant Ratio (5%) e.g. If the LSR (5%) is 1.83, then two means differ significant from one another at $p < 0.05$ if their ratio is larger than 1.83.

Table 7.8 Mean supernatant pH values for all extractants and soils

Soil type	pH	0.01 M $CaCl_2$	1M NH_4NO_3	0.05 M $Ca(NO_3)_2$	1M NH_4OAc	0.05 M $CaCl_2$	1M NH_4Cl	0.04 M EDTA	0.05 M AAAc-EDTA
Patumahoe	5.5	4.97	4.55	4.69	6.55	4.61	4.75	4.95	4.72
	6.0	6.10	6.00	5.90	6.85	5.85	6.10	5.42	4.68
	7.0	6.90	6.85	6.80	7.10	6.75	6.95	6.50	4.65
Te Kuiti	5.5	5.50	5.65	5.42	6.60	5.70	5.05	5.53	4.66
	6.0	6.00	5.85	6.00	6.81	6.00	5.90	5.87	4.65
	7.0	6.70	7.10	6.85	7.00	6.80	6.70	6.80	4.63
Tai Tapu	5.5	5.31	4.62	4.93	6.75	4.71	5.12	4.20	4.60
	6.0	5.90	5.78	6.00	6.90	5.70	5.90	4.73	4.67
	7.0	6.80	6.90	6.65	7.01	6.63	6.92	5.38	4.14

All eight soil extractants, as outlined in Table 7.2, were tested as predictors of plant Cd concentration. The relationships depended upon plant species and extractant used (Table 7.9). AAAc-EDTA, which was a good predictors of plant Cd concentration in the first pot trial (Chapter 6), was less effective in the second pot trial. AAAc-EDTA is an acid extractant (c. pH 4.65), and as discussed was not particularly sensitive to soil pH changes and in some cases extracted significantly greater concentrations of Cd as pH increased (Table 7.7). Sauerbeck and Styperek (1985) found that AAAc-EDTA extracted only slightly less Cd than aqua regia, which was often used as a measure of total soil Cd. He and Singh (1993a) showed than when several soil extractants were tested as predictors of Cd concentration in oat grain, mixed grass, timothy and ryegrass, it was found that when all plant species were analysed together AAAc-EDTA was the only extractant which did not show any significant correlation with plant Cd concentration. Andersson and Nilsson (1974) extracted soil which had been previously limed to give a range of soil pH values 4.8-7.2, with 1 M NH_4OAc (pH 4.8) and 2 M HNO_3 acid. Due to the low pH of the two extractants, they found that the same concentration of Cd was being extracted across all pH levels, and concluded that acid extractants don't give useful information on the plant available concentration of Cd in soil. The same observations and conclusions can be drawn for AAAc-EDTA in the present study.

Some weaker extractants, (0.01 M $CaCl_2$ and 1 M NH_4NO_3) which have low buffering capacity and are sensitive to pH changes and are considered more representative of "real" plant-available metal conditions in soils (Hooda *et al.* 1997) were also shown to be unsuccessful in predicting plant Cd concentrations (Table 7.9). Similarly Bell *et al.* (1997) found no relationship between peanut kernel Cd and 0.1 M $CaCl_2$ extractable Cd, as did Roberts *et al.* (1995) for wheat grain and several vegetable crops using 0.05 M $CaCl_2$. The poor relationship between these 2 extractants and plant Cd concentrations may be a result of the very low Cd concentrations extracted using these reagents and the small number of soils with very different soil properties used in this study.

The more successful predictors of plant Cd concentrations (0.05 M $Ca(NO_3)_2$, 1 M NH_4OAc, 0.05 M $CaCl_2$ and 0.04 M EDTA) appeared to be the reagents which extracted slightly higher concentrations of Cd. However, as found in the evaluation of soil extractants in the first pot trial (Chapter 6), the relationships depended upon individual

Table 7.9 Linear correlation coefficients (r) between concentration of Cd extracted by various reagents and Cd concentration in selected plants species

Extractant	Wheat straw	Wheat grain	Total Wheat	Clover	lettuce	Carrot top	Carrot root	Total carrot	Ryegrass 1	Ryegrass 2	Ryegrass 3	Total Ryegrass
0.01 M $CaCl_2$	0.578n.s	0.496n.s	0.475n.s	0.405n.s	0.487n.s	0.609n.s	0.550n.s	0.463n.s	0.409n.s	0.508n.s	0.639n.s	0.563
1 M NH_4NO_3	0.673*	0.539n.s	0.580n.s	0.412n.s	0.520n.s	0.682*	0.594n.s	0.522n.s	0.519n.s	0.607n.s	0.725*	0.663
0.05 M $Ca(NO_3)_2$	0.518n.s	0.651n.s	0.428n.s	0.542n.s	0.682*	0.796*	0.766*	0.670*	0.689*	0.732*	0.774*	0.778*
1 M NH_4OAc	0.541n.s	0.625n.s	0.489n.s	0.552n.s	0.789*	0.847**	0.850**	0.764*	0.688*	0.753*	0.854**	0.800**
0.05 M $CaCl_2$	0.579n.s	0.617n.s	0.530n.s	0.428n.s	0.694*	0.767*	0.741*	0.648n.s	0.598n.s	0.669*	0.882**	0.733*
1 M NH_4Cl	0.476n.s	0.559n.s	0.435n.s	0.464n.s	0.719*	0.762*	0.789*	0.701*	0.564n.s	0.638n.s	0.780*	0.690*
0.04 M EDTA	0.058n.s	0.010n.s	0.024n.s	0.752*	0.745*	0.680*	0.713*	0.834**	0.686*	0.688*	0.440n.s	0.631n.s
0.05 M AAAc-EDTA	-0.207n.s	-0.105n.s	-0.252n.s	0.660n.s	0.567n.s	0.442n.s	0.498n.s	0.648n.s	0.506n.s	0.457n.s	0.186n.s	0.396n.s

* $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$, n.s not significant

plants and extractants. It was interesting to note that although 1 M NH_4OAc was buffered at pH 7.0, this extractant was a successful predictor of plant Cd concentrations. Andersson and Nilsson (1974) also found 1 M NH_4OAc (pH 7.0) revealed differences in extractable Cd as a function of soil pH.

7.4 Conclusions

The effect of soil pH on plant Cd concentration at low soil Cd concentrations was investigated, along with a re-evaluation of the suitability of 8 soil extractants in predicting Cd concentrations in different plant species. In general, increasing soil pH from 5.5 to 7.0 was found to have a dramatic effect on reducing Cd concentrations in clover, lettuce, carrot and ryegrass, and to a lesser extent in wheat, although the magnitude of reduction varied between plant species and soil types. Soil extractants which were sensitive to soil pH and could extract moderate concentrations of Cd were found to be the most effective in predicting plant Cd concentration (e.g. 0.05 M $Ca(NO_3)_2$, 1 M NH_4OAc, 0.05 M $CaCl_2$ and 0.04 M EDTA). In conclusion, soil pH appears to be a powerful tool in the management of plant Cd concentrations, however its true potential needs to be re-evaluated in a field situation.

Chapter 8

Fractionation of soil cadmium from some New Zealand soils

8.1 Introduction

Cadmium can occur in soils as a free or complexed ion in solution (Tills and Alloway 1983), it may be specifically or non-specifically sorbed onto hydrous oxides, organic matter and clays, (Tiller *et al.* 1984a), as solid phase insoluble precipitates and may occur in solid phase minerals. These discrete chemical forms differ in their solubility and phytoavailablity. Chemical fractionation techniques have been used extensively to fractionate heavy metals such as Cd in soils, in an attempt to determine their distribution between the various forms (McLaren and Crawford 1973b; Tessier *et al.* 1979; Shuman 1985; Mann and Ritchie 1993). For example, Mann and Ritchie (1994) used a fractionation procedure to show that with time, Cd added to soils was transformed to less soluble forms (e.g. oxide and residual bound Cd) and furthermore these transformations were dependent on soil type. Ramos *et al.* (1994) used a sequential fractionation procedure to investigate heavy metal contamination from mining activity. Results indicated that Cd was potentially the most mobile metal while Cu was the least. The advantages and limitations of sequential chemical fractionation techniques have been extensively reported, with a comprehensive summary on the subject provided by Beckett (1989). Regardless of some of the drawbacks, chemical fractionations can provide some very useful information of a metals chemical distribution within a soil, its bioavailability, an indication of the soil as a medium for storing metals, and its leaching potential (Keller and Vedy 1994). Generally, most chemical fractionation schemes separate Cd into exchangeable, organic-bound, oxide-bound and residual fractions.

Whilst the literature indicates that chemical fractionations have been used extensively to study metal distribution in soils, the vast majority of these investigations have involved soils that have been contaminated by sewage-sludge application, mining activity or have had Cd salts added. There have only been a handful of Cd fractionation studies using native soils. The aim of this chapter was to use a chemical fractionation technique to

determine the forms and concentrations of native (or fertiliser derived) Cd in 12 New Zealand topsoils.

8.2 Materials and Methods

8.2.1 Soil preparation and analysis

Twelve topsoil samples (0-150 mm), which differ substantially in their total Cd content, chemical and physical properties were selected for this experiment. The chemical and physical properties of the experimental soils are given in Table 8.1. All soil samples were air-dried and ground to pass through a 2 mm stainless steel sieve prior to laboratory analysis. Soil pH was measured in a water suspension using a soil:solution ratio of 1:2.5. Organic carbon content in the soils was determined by LECO CNS 2000 analyser. Total Cd was determined by a nitric acid microwave digestion method (USEPA SW 846-3051). Cation exchange capacity (CEC) was determined by ammonium acetate leaching at pH 7.0 (Blakemore *et al.* 1987). Amorphous iron (Fe) and aluminium (Al) oxides were determined by ammonium oxalate extraction (Blakemore *et al.* 1987). Crystalline Fe and Al oxides were determined by the oxalate/ascorbic acid extraction method of Shuman (1982), correcting the results for amorphous Fe and Al. Manganese oxide content was determined by extraction with 0.1 M hydroxyl-amine hydrochloride (Shuman 1982), bioavailable P (Olsen P) was determined by bicarbonate extraction (Blakemore *et al.* 1987), and soil texture was determined by the pipette method (Day 1965).

8.2.2 Fractionation procedure

The fractionation procedure used was essentially based on the method of Shuman (1985) (Table 8.2).

(1) Exchangeable Cd

Five grams of soil was shaken with 30 mL 0.01 M $Ca(NO_3)_2$ on an end-over-end shaker for 24 h. The samples were centrifuged for 10 min at 10,000 rpm, (RCF 9, 440 *g*) the supernatant solution filtered through a Whatman No. 42 filter paper, and Cd determined in the filtrate using GFAAS as described above.

(2) Organic Cd

Using a fresh sample, 5 g of soil was weighed into a 100 mL tube, 10 mL of 3% NaOCl added, and the sample heated in water bath at 100°C for 30 min. The sample was then

centrifuged for 10 min at 2000 rpm, the supernatant solution filtered through a Whatman No. 42 filter paper, and Cd was determined in the filtrate using GFAAS, following extraction into MIBK (see 3.11.2). Tube plus wet residue was weighed and 20 mL of fresh 3% NaOCl added and the procedure repeated. Following the second extraction, the soil residue was dispersed in 10 mL deionised water, shaken well and centrifuged at 2000 rpm for 5 min. The supernatant solution was discarded, and the tube plus residue oven dried at 80°C.

(3) Amorphous oxide Cd

Two grams of the oven dried soil from stage (2) was finely ground and shaken with 25 mL of ammonium oxalate on an end-over-end shaker in the dark for 4 h. The sample was centrifuged, at 2000 rpm for 10 min, and the supernatant solution filtered through a Whatman No. 42 filter paper. Cadmium was determined in the filtrate using GFAAS following extraction into MIBK (see 3.11.2). The tube plus wet residue was weighed to enable calculation of the entrained solution.

(4) Crystalline oxide Cd

Twenty-five mL of ammonium oxalate plus ascorbic acid was added to the residue from step (3). This was heated in a boiling water bath for 30 min and the sample centrifuged for 10 min at 2000 rpm, the supernatant solution filtered through a Whatman No. 42 filter paper, and Cd was determined in the filtrate using GFAAS, following extraction into MIBK (see 3.11.2). The soil residue was then dispersed in 10 mL deionised water, shaken well and centrifuged at 2000 rpm for 5 min. The supernatant solution was discarded and the tube plus residue dried at 80°C. The soil was finely ground for the next step.

(5) Residual Cd

One half gram of finely ground soil from step (4) was weighed into a microwave digestion vessel and 10 mL concentrated Aristar HNO_3 acid added. The sample was digested using the USEPA SW 846-3501 programme, and when cool, filtered through a Whatman No 42 filter paper, and made up to a final volume 25 mL. Cadmium was determined in the filtrate using GFAAS as for exchangeable Cd.

Table 8.1 Selected properties of the soils used for chemical fractionation

Soil type	pH	sand	silt	clay	Org. C	Total P	Olsen P	CEC	Mn	Fe		Al		Total Cd
										crystal	amorp	crystal	amorp	
		(%)					($\mu g\ P\ g^{-1}$)	($cmol_c kg^{-1}$)	($\mu g\ g^{-1}$)	(%)				($\mu g\ Cd\ g^{-1}$)
Ohura	5.0	32.4	58.9	8.7	9.6	0.149	4	6.3	74.0	0.28	0.95	0.04	2.09	0.31
Te Kuiti	4.9	24.9	45.3	29.8	13.0	0.291	13	9.2	620.0	0.19	0.80	0.32	3.10	1.34
Whakatane	5.2	47.9	34.4	17.7	6.7	0.264	117	10.8	162.3	0.41	0.59	0.12	0.27	0.74
Taupo	4.8	61.6	23.4	15.0	8.3	0.138	9	8.7	246.1	0.43	0.36	0.12	0.77	0.45
Temuka	5.2	14.2	61.2	24.6	5.5	0.085	6	14.6	50.4	0.24	0.95	0.20	0.16	0.18
Waimakariri	4.9	40.2	47.7	12.2	2.4	0.103	23	4.5	31.3	0.70	0.17	0.23	0.09	0.07
Summit	5.0	17.2	80.7	2.1	4.7	0.082	16	9.2	161.6	0.72	0.24	0.27	0.12	0.03
Waiareka	6.1	19.3	17.2	33.4	4.9	0.132	51	22.9	338.0	0.15	0.88	0.11	0.18	0.13
Tai Tapu	5.5	27.9	32.8	39.3	3.6	0.103	45	11.1	56.5	0.77	0.28	0.27	0.16	0.19
Temuka	5.4	16.1	54.5	29.4	2.6	0.063	15	11.8	113.0	0.53	0.44	0.25	0.11	0.13
Patumahoe	5.4	22.5	71.2	6.3	7.4	0.171	17	10.8	170.0	0.88	0.68	0.68	2.30	0.78
Lismore	4.9	45.0	30.0	24.0	3.8	n.d	n.d	13.6	n.d	n.d	n.d	n.d	n.d	0.04

n.d not determined

Table 8.2 Sequential fractionation procedure for cadmium in soil

Step	Fraction	Solution	Soil (g)	Solution (mL)	Conditions
1	Exchangeable	0.01 M $Ca(NO_3)_2$	5	30	shake 2 h
2	Organic matter	3.5% NaOCl (pH 8.5)	5	10	boiling water bath 30 min (repeat once)
3	Amorphous iron oxide	0.2 M $(NH_4)_2C_2O_4.H_2O$ + 0.2 M $H_2C_2O_4$ (pH 3)	2	25	shake 4 h in the dark
4	Crystalline iron oxide	0.2 M $(NH_4)_2C_2O_4.H_2O$ + 0.2 M $H_2C_2O_4$ (pH 3) + 0.1 M ascorbic acid	2	25	boiling water bath 30 min
5	Residual	Concentrated HNO_3 acid	0.5	10	microwave digestion

8.3 Results and discussion

8.3.1 Soils

Table 8.1 shows that total soil Cd concentrations ranged from 0.03 to 1.34 μg Cd g^{-1} soil. Results of a national survey examining the Cd status of native and pastoral soil sites indicates that the mean Cd concentration for native soil sites was 0.20 mg kg^{-1}, while the average total Cd concentration for soils where phosphate fertiliser had been applied was 0.44 mg kg^{-1} (Roberts *et al.* 1994). Total Cd concentrations in this study indicate that more than half the soils analysed have Cd at background concentrations (i.e. < 0.2 mg kg^{-1}) while the others have elevated Cd concentrations as a result of phosphate fertiliser addition.

8.3.2 Cadmium fractions

As a check on the fractionation procedure, the sum of the individual fractions was plotted against the total soil Cd (Fig 8.1). Results shows a satisfactory agreement ($r^2 = 0.95$ $p < 0.05$) between the total soil Cd values and the sum of Cd extracted in the individual fractions, despite the fact that total Cd concentrations were very low (less than 1.4 μg Cd g^{-1}).

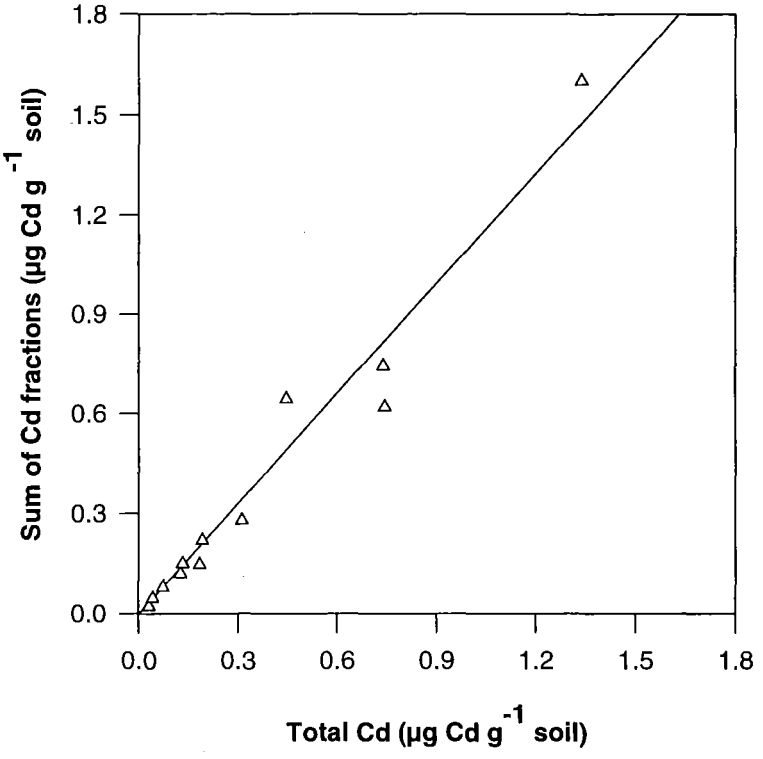


Fig. 8.1 Comparison of total Cd values with the sum of the individual fractions.

The concentrations and percentages of total Cd extracted from individual fractions from the soils studied are presented in Tables 8.3 and 8.4 respectively. There was a large range in Cd concentrations extracted in individual fractions. For all soils studied, the smallest concentrations of Cd were found in the exchangeable fraction (Table 8.4), whilst the largest concentrations of Cd were associated with the residual and organic fractions. Cadmium associated with the two oxide fractions were relatively low. The mean concentrations of Cd present in the different fractions (Table 8.5) decreased in the order: residual > organic >> amorphous oxide > crystalline oxide > exchangeable.

Berti and Jacobs (1996) have highlighted the fact that comparison of fractionation data between studies is often complicated, given that the nature of Cd added to soils is often very different (i.e. native, sludge or salt amended soils) and also very different sequential

Table 8.3 Mean concentrations (μg kg^{-1} soil) of soil Cd in individual fractions

Soils	Cadmium in soil fractions (μg Cd kg^{-1} soil)						
	Exchangeable	**Organic**	**Amorphous oxide**	**Crystalline oxide**	**Residual**	**Sum**	**Total**
Ohura	21.0	113.0	30.0	14.9	100.0	279	312
Te Kuiti	35.1	414.0	155.5	84.2	912.0	1600	1338
Whakatane	23.8	397.0	50.0	31.5	241.0	743	741
Taupo	15.1	152.0	35.1	20.4	421.0	644	447
Rakaia	2.2	38.7	7.7	5.4	92.0	146	183
Temuka	5.4	21.6	1.7	4.2	47.1	80	74
Summit	1.0	8.5	1.9	1.5	9.1	22	31
Waiareka	1.0	73.7	10.0	5.5	29	119	125
Tai Tapu	4.5	94.5	10.1	6.3	103.0	218	193
Temuka	3.9	92.9	7.1	4.9	40	149	132
Patumahoe	29.6	311.9	79.3	3.9	195.0	620	744
Lismore	0.5	9.3	9.4	11.7	15.8	47	42

fractionation techniques are employed. This study fractionated Cd that was in background concentrations or has accumulated in soils as a result of phosphate fertiliser application during a period of many years. This may be very different to Cd added to soil in the form of soluble salts (e.g. $CdCl_2$ Bell *et al.* 1991) or sewage sludge.

The present study revealed that a substantial proportion (85%) of Cd is present in the residual and organic fractions and only small proportion were present in the exchangeable and the two oxide fractions. The low concentration of Cd in exchangeable forms has been reported for other studies. Krishnamurti *et al.* (1995a) for example used a fractionation scheme to investigate native Cd in 16 surface soils from Saskatchewan. As in the present study, exchangeable Cd was found to be negligible using 1 M $Mg(NO_3)_2$ as an extractant. Chang *et al.* (1984), who studied the chemical forms of heavy metals in sludge treated soils by sequential fractionation, also found that Cd associated with the exchangeable and adsorbed fractions were negligible. In contrast, in an investigation of three soils and a harbour sediment that were considered highly contaminated, Hickey and Kittrick (1984) found that the greatest concentrations of Cd were in the first fraction (1 M $MgCl_2$, pH 7) (mean value of 37%). Similarly, Sloan *et al.* (1997), showed that biosolids applied Cd were in forms that were easily extracted from soils, with 75% of the total soil Cd in

Table 8.4 Proportions of soil Cd in individual soils fraction

	Cadmium in soil fractions (% of sum total)				
Soils	**Exchangeable**	**Organic**	**Amorphous oxide**	**Crystalline oxide**	**Residual**
Ohura	7.5	40.5	10.8	5.4	35.9
Te Kuiti	2.2	25.9	9.7	5.3	56.9
Whakatane	3.2	53.4	6.7	4.2	32.4
Taupo	2.3	23.7	5.4	3.2	65.4
Rakaia	1.5	26.5	5.2	3.7	63.0
Temuka	6.8	27.0	2.1	5.3	58.9
Summit	4.7	38.6	8.5	6.8	41.3
Waiareka	0.9	61.7	8.4	4.6	24.3
Tai Tapu	2.1	43.3	4.6	2.9	47.1
Temuka	2.1	62.4	4.6	3.3	26.8
Patumahoe	2.65	50.3	12.8	0.6	31.5
Lismore	1.1	19.9	20.1	25.1	33.8

Table 8.5 Ranges, proportional ranges and means of soil Cd in individual fractions

	μg Cd kg^{-1} soil			% of total		
Fraction	Range		Mean	Range		Mean
Exchangeable	0.5 -	35.1	11.9	0.9 -	7.5	3.1
Organic	8.5 -	414.0	143.9	23.7 -	62.4	39.4
Amorphous	1.7 -	155.0	33.2	2.1 -	20.1	8.2
Crystalline	1.5 -	84.0	16.2	0.6 -	25.1	5.9
Residual	9.1 -	912.0	183.8	24.3 -	65.4	43.1

exchangeable or specifically sorbed fractions. Berti and Jacobs (1996) in soils amended with sludge containing up to 2.2 μg Cd g^{-1}, could only detect Cd in the exchangeable (0.5 M $Ca(NO_3)_2$) and acid soluble (0.44 M CH_3COOH + 0.1 M $Ca(NO_3)_2$) fractions. While Bell *et al.* (1991), found that up to 60% of Cd added to soils as either a salt or sludge was found in the exchangeable/organically complexed fractions. Ramos *et al.* (1994) found that the distribution of Cd in the various soil fractions was dependent on the total metal content of the soil. While significant concentrations of Cd in exchangeable forms were

found in mine contaminated soils, Cd was not detected in the exchangeable fractions on less polluted soils sites, with Cd mainly associated with the carbonate fraction. It appears therefore that the proportions of Cd in exchangeable forms will depend on the form in which Cd has been applied to the soil, the degree of level contamination, the soil type and the length of time the metal has been in the soil.

Results for the present study indicate that a large proportion of Cd is associated with the organic fraction, with a mean value of (39%). The large proportion of Cd in the organic fraction compliments the findings of Chapter 4 and 5 in relation to the importance of organic carbon in controlling solubility, sorption and desorption of Cd. The soils studied have medium to high organic carbon contents for New Zealand (Blakemore *et al.* 1987) which may indicate why this fraction is important.

There was a large range in the proportion of Cd in the residual fraction ranging from 24% for the Waiareka soil to 65% for the Taupo soil with a mean value of (43%). Gibson and Farmer (1986) observed up to 42% of the total Cd in the residual fraction of contaminated soils. Whereas, Ma and Rao (1997) found that with the exception of two soils, more than 91% of the total Cd in all soils was associated with the residual fraction. Chang *et al.* (1984) found that Cd was mainly in carbonate and residual forms in the soils studied. While, Warren (1996) showed that Cd associated with the residual fraction was the most important fraction in a stony forest soil. McLaren and Crawford (1973b), and Shuman (1985) have reported that the highest concentrations of metals are generally found in the primary and secondary minerals of the residual fraction. These studies, like the present one were analysing native metal concentrations. In contrast, Keller and Vedy (1994) found only 10 - 26% of Cd resided in the residual fraction in two forest soils. Sloan *et al.* (1997), found that < 10% of Cd in the residual fraction, even after 15 years after biosolid application ceased. Similarly, Hickey and Kittrick (1984) found that Cd was lowest in the residual fraction of contaminated soils.

Results indicate that Cd was mainly in the residual and organic soil fractions, with only small concentrations in readily available forms. It appears there are no particular trends in

the distribution within the Cd fractions with regard to whether Cd is geogenic or anthropogenic in origin.

8.3.3 Relationships between Cd fractionation and Cd phytoavailability

When the concentrations of Cd associated with individual Cd fractions were related to the 8 soil extractants which were evaluated in Chapters 6 and 7 as a measure of Cd phytoavailability, it was found that no one fraction was significantly better related to a soil extractant than another. This possibly indicates that the distribution of Cd in individual fractions in the soils studied was dependent on the total Cd content of the soil. This indeed appeared to be the case, with significant relationships ($p < 0.001$) between total Cd, individual soil fractions and soil extractants (Table 8.6).

Table 8.6 Linear correlation coefficients (r) between total Cd concentration and soil extractants and Cd fractions

	Total Cd
0.01 M $CaCl_2$	0.921***
1 M NH_4NO_3	0.941***
0.05 $Ca(NO_3)_2$	0.892***
0.05 M $CaCl_2$	0.820***
1 M NH_4OAc	0.856***
1 M NH_4Cl	0.949***
0.04 M EDTA	0.881***
0.05 M AAAc-EDTA	0.967***
exchangeable fraction	0.903***
organic fraction	0.902***
amorphous oxide fraction	0.978***
crystalline oxide fraction	0.984***
residual fraction	0.974***

* $p < 0.05$; ** $p < 0.01$; *** $p < 0.001$; n.s., not significant

When the concentration of Cd extracted from the exchangeable and organic fractions were added together and compared to the concentration of EDTA (ethylene diamine tetraacetic acid) extractable Cd, it was found there was a highly significant relationship (Fig 8.2). Mann and Ritchie (1993) found that EDTA not only extracts Cd from soluble and exchangeable soil sites, but also Cd from strongly bound oxide sites. Likewise Ure *et al.* (1993) indicate that EDTA can extract Cd from oxide sites, as well as organically and

carbonate bound Cd. Results in this study therefore confirm that EDTA may not extract exchangeable Cd but Cd associated with organic matter.

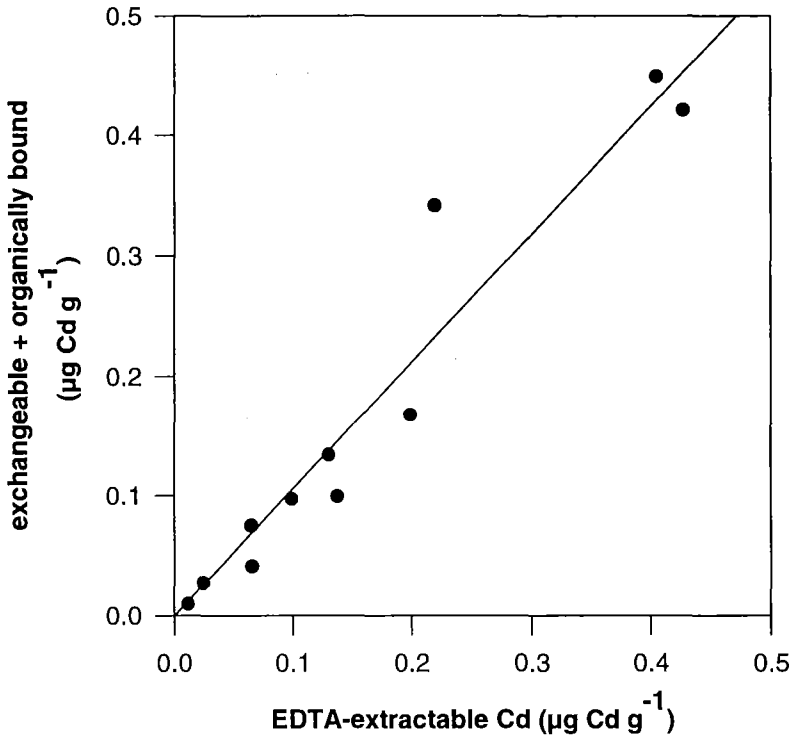


Fig. 8.2 Relationship between EDTA-extractable Cd and the sum of exchangeable and organically bound Cd for 12 soils.

Similarly the concentration of Cd extracted with AAAc-EDTA (acid ammonium acetate-ethylene diamine tetraacetic acid) was related to the sum of Cd extracted in the first four steps in the fractionation, indicating this extractant can solubilise oxide material (Fig 8.3).

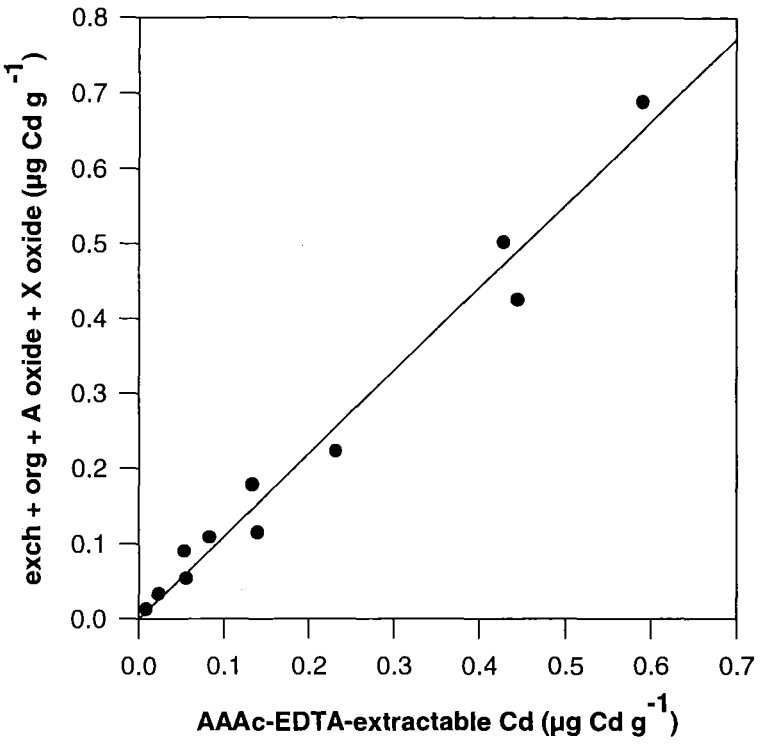


Fig. 8.3 Relationship between AAAc-EDTA-extactable Cd and the sum of exchangeable, organic and oxide bound Cd for 12 soils.

8.4 Conclusions

The distribution of native Cd was investigated using a sequential fractionation procedure for 12 different New Zealand topsoils. Results showed there was a wide range in the concentrations of Cd associated with individual soil fractions. The greatest concentration of Cd was associated with the organic and residual fractions, while the lowest concentration of Cd was in exchangeable forms. Results indicated that a substantial proportion of Cd added to the soil from fertiliser application ended up residing in the residual fraction of the soils studied. This suggest that a large proportion of native soil Cd in these soils is in forms likely to be slowly unavailable for plant uptake. There is evidence to suggest that soil extractants that are commonly used to determine plant Cd concentrations (i.e. EDTA, AAAc-EDTA) extracted Cd from soil non-exchangeable forms.

Chapter 9

Effect of long-term phosphatic fertiliser applications on the amounts and forms of cadmium in soils under irrigated pasture in New Zealand

9.1 Introduction

Reports in the literature have indicated that soil Cd concentrations and the amount of superphosphate fertiliser added to soil are strongly related (Williams and David 1973; 1976; Rothbaum *et al.* 1986). The Cd content of phosphate fertilisers will vary depending upon the source of the raw rock phosphate used in its manufacture. In New Zealand, up until the mid-80's, the main source of rock phosphate used in phosphate fertiliser manufacture was from oceanic sedimentary and guano-based deposits, with Cd concentrations ranging between 34 - 69 mg kg^{-1} (Rothbaum *et al.* 1986). By international standards these are considered high Cd phosphate rocks. A recent national survey examining the Cd status of pastoral (fertilised) versus native (unfertilised) soil sites indicated that on average, total soil Cd concentrations at pastoral sites were double those of their native counterparts, with total soil Cd highly correlated with total soil phosphorus (P) (Roberts *et al.* 1994). The accumulation of Cd in soils from the long-term application of phosphatic fertilisers has been well documented in studies in many countries (Mulla *et al.* 1980; Mordvedt *et al.* 1981; Isermann 1982; Kofoed and Klausen 1983; Rothbaum *et al* 1986; Baerug and Singh 1990; Andersson and Siman 1991; Singh 1991). However in New Zealand only limited research has been conducted into the long-term accumulation of Cd in soils (Rothbaum *et al.* 1986; Loganathan *et al.* 1995; Loganathan *et al.* 1997). In addition, recent information from Hamon *et al.* (1997) suggests that some 'fixation' of Cd added to soils occurs, as do studies by Ainsworth *et al.* (1994) for synthetic hydrous iron oxides and for soil clays McLaren *et al.* (1998). There is also evidence from Gray *et al.* (1998) which supports the possibility of Cd fixation processes occurring in New Zealand soils. Thus, the rate of Cd accumulation in soils and its subsequent immobilisation are both important factors which influence to Cd phytoavailability.

In 1952, a comprehensive field trial was set up at Winchmore Irrigation Research Station in Canterbury, New Zealand to determine the long-term phosphorus fertiliser requirements of

intensively grazed irrigated pasture. Soil samples have been collected since the beginning of the trial in 1952, which provide an excellent opportunity to investigate the rate of Cd accumulation. This trial also has plots where the effect of Cd residence time could be estimated from soils where Cd has been added to soils followed by a period of no fertiliser application. This chapter presents the findings of an investigation into the rate of Cd accumulation, Cd bioavailability, and Cd distribution within the soil.

9.2 Materials and methods

9.2.1 Soil

Soil samples were obtained from the long-term superphosphate trial at the Winchmore Irrigation Research Station. The soil at Winchmore is a Lismore silt loam (Orthic Brown Soil); a moderately weathered, shallow, free-draining soil derived from accumulations of greywacke alluvium and loess (Table 9.1).

Table 9.1 Selected physical and chemical characteristics of the native Lismore silt loam (Orthic Brown Soil) at Winchmore (NZ Soil Burea 1968)

	Soil Depth 0 - 75 mm
pH (dried soil, H_2O)	4.9
pH (dried soil KCl)	4.2
dry bulk density (g cm^{-3})	1.16
CEC ($cmol_c$ kg^{-1})	13.6
base saturation (%)	38.0
organic carbon (%)	3.8
sand (%)	45.0
silt (%)	30.0
clay (%)	24.0

9.2.2 Trial set-up

The site on which the long-term superphosphate trial is situated was originally under unfertilised browntop (*Agrostis capillaris*) pasture. In 1948, the browntop pasture was ploughed up and the site prepared for border-dyke irrigation, which involved subdivision of the trial into 20 separately fenced, separately irrigated borders (0.08 ha). In 1950, a new perennial ryegrass (*Lolium perenne*)/white clover (*Trifolium repens*) pasture was sown prior to the start of the long-term trial in 1952. During site preparation (i.e. 1948-1952), 420 kg ha^{-1} superphosphate and 4 t ha^{-1} lime ($CaCO_3$) was applied to the trial area.

The long-term trial incorporated five different treatments (control, 188PA, 376PA, 376R and 564R), where the numbers indicate the superphosphate application rate (kg ha^{-1} $year^{-1}$) either added yearly (PA) or in the years 1952-1957 only (R) (Table 9.2). Four replicates of each treatment were arranged in a randomised complete block design, and each treatment was grazed rotationally by a separate flock of dry ewes and plots irrigated as required 4 - 5 times per year. In 1972, 4 t ha^{-1} lime was applied to the trial area to maintain soil pH above 6.

Table 9.2 Treatments for the long-term superphosphate trial at Winchmore

Key	Treatment
control	no superphosphate applied
188 PA	188 kg single superphosphate applied annually since 1952
376 PA	376 kg single superphosphate applied annually since 1952
376 PA	376 kg single superphosphate applied annually between years 1952 - 1957
564 PA	564 kg single superphosphate applied annually between years 1952 - 1957

9.2.3 Soil samples

Three types of samples were collected from the trial. Composite topsoil (0-75 mm) samples were taken from each of the four replicates of the control, 188PA, 376PA treatments for the years 1952, 1958, 1964, 1971, 1974, 1979, 1985, 1989, 1996. Samples were also taken to a depth of 150 mm at 50 mm intervals for the control, 188PA, 376PA treatments in 1995. Soil samples were also taken from the 376R and 564R treatments in 1958, the first year after superphosphate fertiliser application ceased and from the same plots again 21 years later in 1979.

9.2.4 Analysis

9.2.4.1 Soil

All samples were analysed for total Cd by a nitric acid microwave digestion (USEPA SW 846-3051) and extractable Cd by 0.04 M EDTA for 2 h at 20 °C (McLaren *et al.* 1984). Cadmium was measured by graphite furnace atomic absorption spectrophotometry (GFAAS) with deuterium background correction using a 0.1% H_3PO_4 modifier. Samples that were taken to depth (control, 188PA, and 376PA treatments in 1995) and samples from the 376R and 564R treatments in 1958 and 1979 were also subjected to a sequential

desorption procedure. Desorption of Cd was determined by repeated equilibration of soil samples (5.0 g) with 30 mL of 0.01 M $Ca(NO_3)_2$. Equilibrations were carried out for 2 h at 20 °C. This desorption period was selected as a result of a preliminary study which showed little change in the amount of Cd desorbed from the soil after a 2 h equilibration (refer section 4.3.2.2). Following equilibration, samples were centrifuged at 10,000 rpm (RCF 9,440*g*) for 10 minutes, and the supernatant decanted filtered through a Whatman No. 42 filter paper and Cd determined as described above. The soil residue was then resuspended in fresh 0.01 M $Ca(NO_3)_2$, and the procedure repeated five times.

Samples taken from the years 1952, 1971, 1979 and 1996 from the control, 188PA and 376PA treatments, and samples from 1958 and 1979 from the 376R and 564R treatments, were subjected to a sequential extraction procedure. The Winchmore soil has low Mn oxides and lacks carbonates, therefore a technique was adopted that fractionated Cd into five different fractions; exchangeable, organic, amorphous Fe/Al oxide, crystalline Fe/Al oxide and residual (Table 9.3). The fractionation procedure is the same as outlined in Chapter 8.

Table 9.3 Sequential fractionation procedure for cadmium in soil

Step	Fraction	Solution	Soil (g)	Solution (mL)	Conditions
1	Exchangeable	0.01 M $Ca(NO_3)_2$	5	30	shake 2 h
2	Organic matter	3.5% NaOCl (pH 8.5)	5	10	boiling water bath 30 min (repeat once)
3	Amorphous iron oxide	0.2 M $(NH_4)_2C_2O_4.H_2O$ + 0.2 M $H_2C_2O_4$ (pH 3)	2	25	shake 4 h in the dark
4	Crystalline iron oxide	0.2 M $(NH_4)_2C_2O_4.H_2O$ + 0.2 M $H_2C_2O_4$ (pH 3) + 0.1 M ascorbic acid	2	25	boiling water bath 30 min
5	Residual	Concentrated HNO_3 acid	0.5	10	microwave digestion

9.2.5 Statistical analysis

All statistical analysis was carried out using the SYSTAT package.

9.3 Results and discussion

9.3.1 Temporal trends in soil Cd

The concentration of Cd in soils from the long term superphosphate trial is shown in Fig 9.1. It indicates that over a period of 44 years of superphosphate application, there was a significant increase in the concentration of Cd on the fertilised plots relative to the control. Olsen P, a measure of bioavailable phosphorus, also shows a similar increase on the two fertilised treatments compared to the control treatment during the course of the trial (Fig 9.2) (Metherell pers comm.).

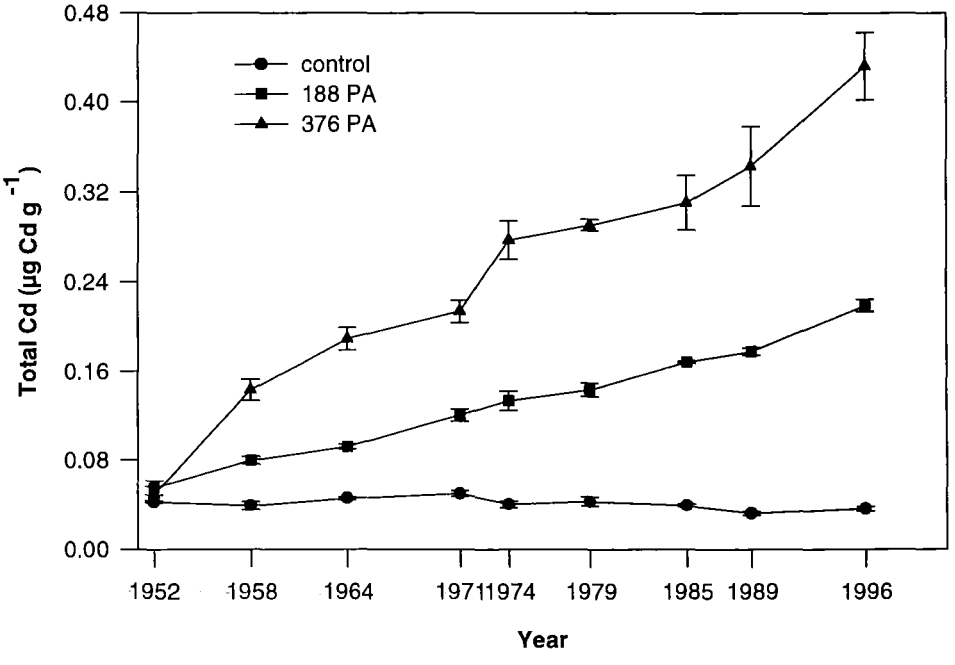


Fig. 9.1 Total Cd concentrations (µg Cd g^{-1}) on different fertiliser treatments in the Winchmore long-term trial between 1952-1996. Bars denote 95% CI.

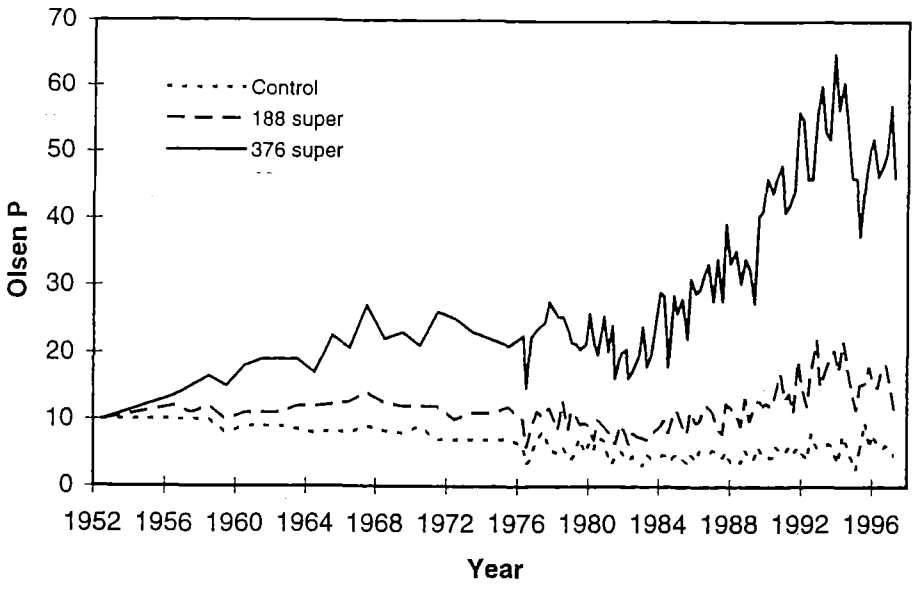


Fig. 9.2 Concentrations of Olsen P from (control, 188PA and 376PA) treatments on the Winchmore long-term phosphate trial between 1952-1996.

Total Cd concentration on the control plot has decreased slightly (although not statistically significant) during the course of the trial from 0.043 μg Cd g^{-1} in 1952 to 0.036 μg Cd g^{-1} in 1996. The decrease in soil Cd concentration is likely to be a function of Cd that was present in the initial superphosphate application during the trial establishment being lost from the soil, by leaching and/or animal products. The slight decrease in Cd on the control plot also suggests that there were no measurable inputs of atmospheric Cd to the soil. Atmospheric inputs of Cd to soil have been shown in a number of European countries to be significant, with values for rural areas ranging between 1 - 5 g ha^{-1} yr^{-1} (Hovmand 1981; Tjell *et al.* 1981; Hutton and Symon 1986; Jones *et al.* 1987). The amount of Cd deposited onto a soil is dependent on the proximity to a source of Cd emission. The major sources of atmospheric pollution are from high temperature industrial processes (e.g. non-ferrous metal production, coal and oil combustion and municipal and sewage sludge incineration) which were absent from the vicinity of the trial site.

On the two fertilised treatments, there was a significant ($p < 0.001$) increase in Cd concentrations with time. Total Cd on the 188PA treatment increased from 0.055 to 0.219 μg Cd g^{-1}, whereas total Cd increased from 0.049 to 0.432 μg Cd g^{-1} on the 376PA treatment between 1952 and 1996. This upper value for the 376PA treatment corresponds closely to the mean Cd concentration determined for fertilised pasture soils in New Zealand

of 0.44 μg Cd g^{-1} reported by Roberts *et al.* (1994). As expected the 376PA treatment accumulated approximately twice as much Cd as did the 188PA treatment.

The rate of Cd accumulation calculated for the high fertiliser (376PA) treatment, (g ha^{-1} yr^{-1} to a soil depth of 75 mm calculated using a bulk density of the unimproved trial soil (Table 9.1) was estimated at 7.8 g ha^{-1} yr^{-1}. This figure assumes there has been no Cd losses through plant or animal uptake and leaching. A direct comparison of this value to other referenced studies in New Zealand and overseas, is complicated by the fact that often different sampling depths are quoted, differing amounts of P fertiliser from different rock P sources have been applied to soil, soil inherently has different chemical and physical properties which affect sorption, leaching etc, and methods for total Cd determination vary between studies.

Data from Loganathan *et al.* (1995) was used to calculate Cd accumulation for a grazed hill pasture trial, which has received the equivalent of 425 kg single superphosphate ha^{-1} yr^{-1} for 20 yr. An accumulation rate of between 11.3 g ha^{-1} yr^{-1} for the high slopes and 17.8 g ha^{-1} yr^{-1} for the low slopes (0 - 150 mm) was determined. The larger value for the low slope was attributed to greater amounts of fertiliser input per unit land area and higher amounts of Cd returned in animal excreta. The values are higher than the figure calculated for the present study, which may reflect differences in superphosphate application (i.e. 425 versus 376 kg ha^{-1} yr^{-1}). Furthermore, the soil carbon levels on this soil are between 7.1 - 9.0%, which are significantly higher than carbon levels found at the Winchmore trial, and may contribute to sorption of Cd in this soil. In a more recent study by Loganathan *et al.* (1997) which investigated the effect of phosphate fertiliser type on accumulation and plant availability of Cd in grassland soils, Cd accumulation rates of 7.8 and 13.4 g ha^{-1} yr^{-1} (0 - 75 mm) were calculated for the 30 and 60 kg ha^{-1} yr^{-1} SSP treatments. These soil concentrations accounted for 80 and 69% respectively of the total Cd applied through fertiliser application. Moreover, Cd recovery by pasture species accounted for less than 2 % of the Cd applied as fertiliser for these two treatments, which may indicate that there has been Cd losses through leaching from this soil. Rothbaum *et al.* (1986) calculated an annual Cd accumulation rate of 6 g ha^{-1} (0-10mm), for a long-term (30 yr) phosphate trial on pasture in Papatoetoe, New Zealand. Furthermore, results indicated that only about one

half of the applied Cd could be accounted for, which was suggested to have been loss through leaching from this soil. In an overseas study, Johnston and Jones (1995) showed annual increases of 7.2 g ha^{-1} yr^{-1} for a 100 yr old superphosphate trial on pasture at Rothamsted, United Kingdom. However, the authors highlight the importance of atmospheric inputs of Cd which reduced annual inputs from superphosphate to approximately 4 g ha^{-1}.

EDTA extractable Cd, which has been used widely to predict of Cd phytoavailability (Jackson and Alloway 1991), was also determined for samples from the trial. As for total Cd, during the course of the trial there was a significant ($p < 0.001$) increase in Cd at both the 188 and 376PA fertiliser treatments relative to the control (Fig 9.3).

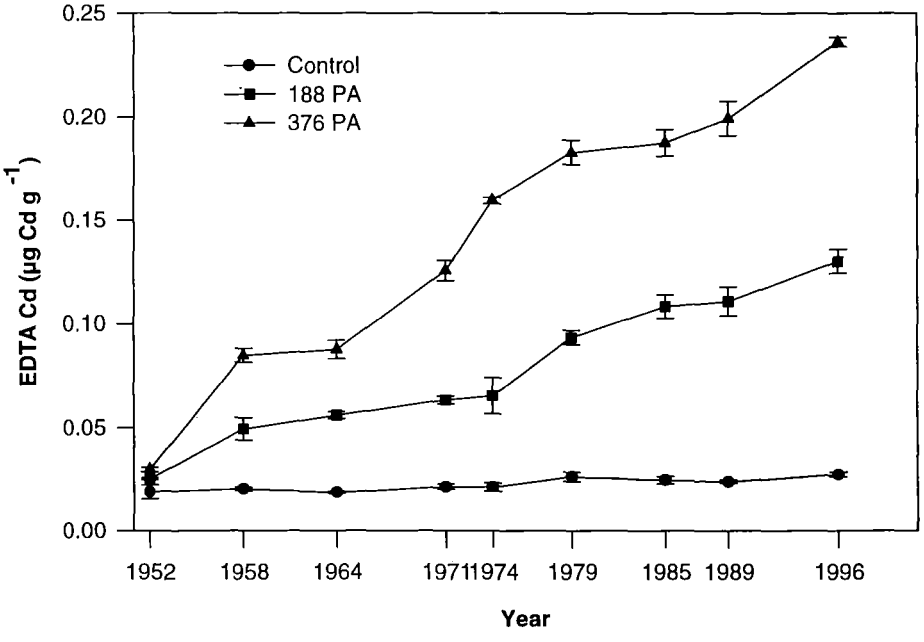


Fig. 9.3 EDTA-extractable Cd concentrations (µg Cd g^{-1}) on the different fertiliser treatments in the Winchmore long-term trial between 1952-1996. Bars denote 95% CI.

EDTA-extractable Cd for the 188PA treatment increased from 0.025 to 0.130 µg Cd g^{-1}, whereas for the 376PA treatment, EDTA extractable Cd concentrations increased from

0.030 to 0.236 μg Cd g^{-1}. The control treatment has remained fairly constant at 0.019 to 0.025 μg Cd g^{-1}. Similarly, the 376PA treatment, as for total Cd, accumulated twice as much Cd as the 188PA treatment, with EDTA extracting approximately 60% of the total soil Cd.

9.3.2 Cadmium fractionation

The concentration of Cd extracted (μg Cd kg^{-1}) associated with each soil fraction for the three treatments (control, 188PA, 376PA) and for four sampling periods (1952, 1971, 1979, 1996) are presented in Fig 9.4. Results indicate that for the fertilised treatments, there has been an increase in the concentration of Cd associated with each fraction during the course of the trial. While for the control treatment, there was been no significant change with time.

When the concentrations of Cd extracted in the control treatments for each sampling period are subtracted from the fertilised treatments, the concentration of 'fertiliser derived' Cd in each fraction can be estimated. This is shown in Table 9.4, where the concentration of Cd in each fraction is expressed as a percentage of total fertiliser added Cd for the two treatments for the years 1971, 1979 and 1996. The main feature of these results is the large proportion of Cd associated with the organic (28 - 63%) and residual (25 - 47%) fractions. Results clearly show that a substantial proportion of added Cd to this soil has ended up residing in the residual fraction, which is considered unavailable to plants. In addition, a large percentage of added Cd is associated with the organic fraction, while the concentrations of Cd in the other fractions have remained relatively low.

Table 9.4 Percentage Cd in each fraction as a total of 'fertiliser added' Cd for 188PA and 376PA fertiliser treatments for 1971, 1979 and 1996

	1971		1979		1996	
	188	376	188	376	188	376
Exchangeable	5.9	5.8	2.6	2.8	5.4	5.4
Organic	28.1	29.7	62.9	51.4	43.9	53.3
Amorphous	13.8	8.5	6.8	7.1	18.5	10.2
Crystalline	5.4	8.6	2.8	3.7	7.5	5.1
Residual	46.8	47.4	24.9	34.9	24.6	26.2

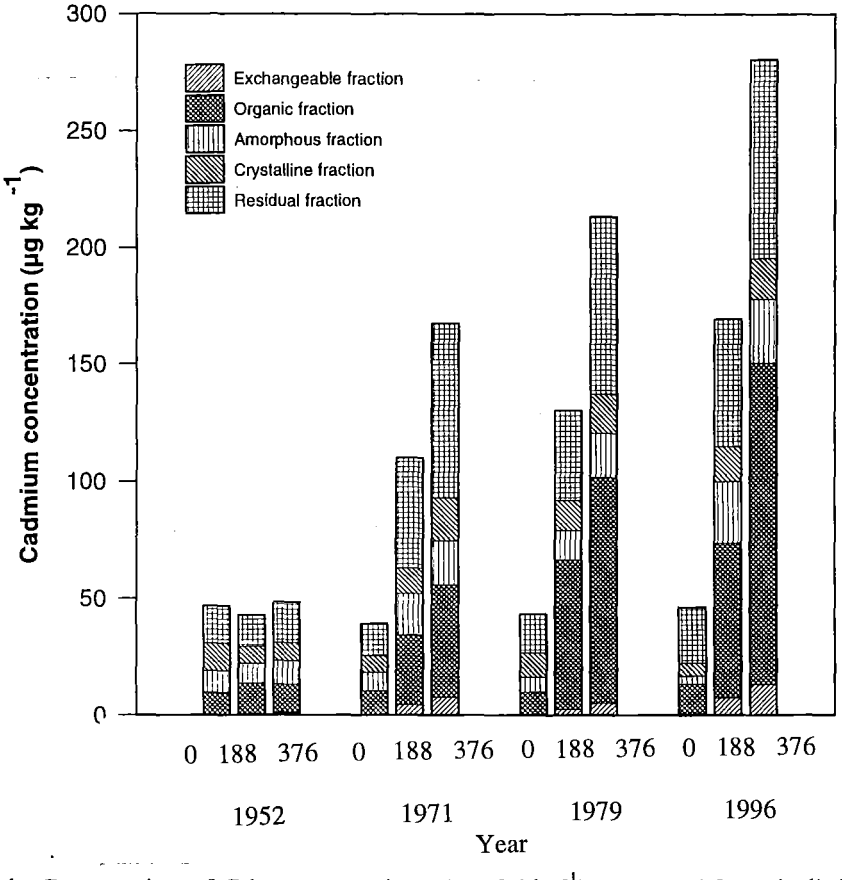


Fig. 9.4 Comparsion of Cd concentrations (µg Cd kg^{-1}) extracted from individual soil fractions for the (control, 188PA, 376PA) treatments for the years 1952, 1971, 1979, and 1996.

Fig 9.5 a - e shows Cd associated with each soil fraction for the three treatments and sampling periods, presented this time as a percentage of total soil Cd (native + fertiliser added). Looking at the overall trends in Cd fractions with time (Fig 9.5 a-e), there were significantly greater proportions of Cd associated with the residual and organic fractions compared to the oxide fractions, with by far the lowest concentrations of Cd in the exchangeable fraction. There was no significant change in the percentage of Cd associated with the exchangeable (Fig 9.5 a) or organic fractions (Fig 9.5 b) during the course of the trial on the control treatment. However, there was a decrease in Cd associated with both the oxide fractions (Fig 9.5 c,d), and a corresponding increase in the percentage

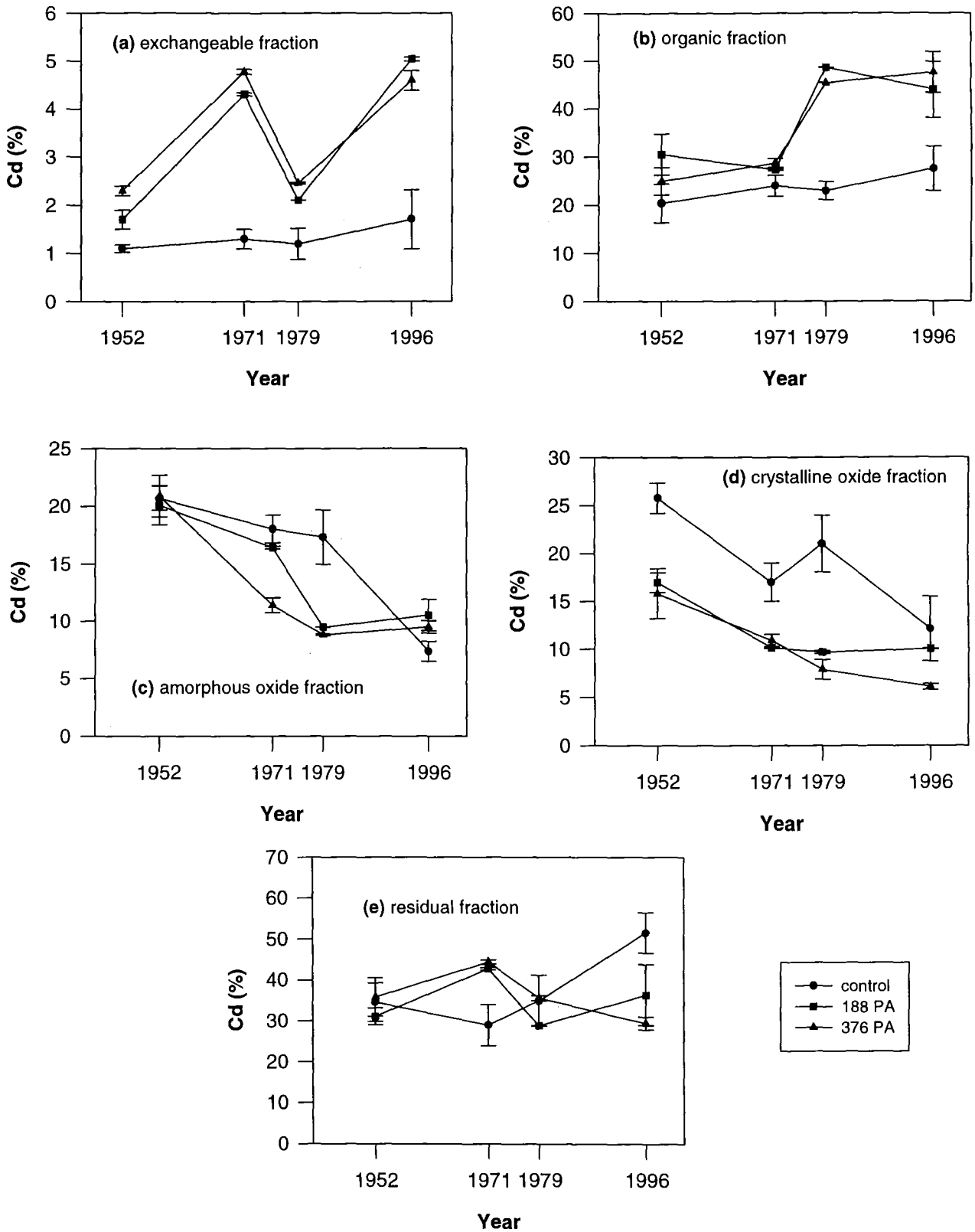


Fig. 9.5a-e A comparison of the % Cd extracted from (a) exchangeable, (b) organic, (c) amorphous oxide, (d) crystalline oxide and (e) residual fractions from the Winchmore trial in the years 1952, 1971, 1979 and 1996. Bars denote 95% CI.

concentration of Cd associated with the residual fraction (Fig 9.5 e). There were significant increases in the percentage of exchangeable Cd for the 188PA treatment from 1952 to 1996, although there appeared to be a decrease in 1979 (Fig 9.5a). There was a significant increase in Cd associated with the organic fraction with time (Fig 9.5b). Similar to the control treatment, Cd associated with the two oxide fractions decreased (Fig 9.5 c,d) during the course of the trial, with no significant change in the residual Cd fraction (Fig 9.5 e). There was a significant increase in exchangeable Cd from 1952 to 1996 for the 376PA treatment, similar to the 188PA treatment, although there was again a decrease in 1979 (Fig 9.5a). There was a significant increase in Cd associated with the organic fraction with time (Fig 9.5b). Similarly to the control treatment, Cd associated with the two oxide fractions decreased (Fig 9.5 c,d) with a slight decrease in Cd in the residual fraction (Fig 9.5 e).

The increase in the concentration of exchangeable and organically bound Cd compared to the control may be a result of an increase in the organic carbon levels in the soil, which have significantly ($p < 0.05$) increased in the fertilised plots from 2.8 % in 1952 to 4.2% in 1996. This increase in organic carbon would have provided additional sorption sites for Cd added in superphosphate. This may partly explain the decrease in Cd associated with the residual fractions with time (Table 9.4). In addition, with increased Cd loading, the limited oxide sites, may have become saturated, and as a consequence Cd has become sorbed and/or redistributed to less strongly bound organic and exchangeable sites with time. The decrease in the percentage of Cd in the exchangeable fraction in 1979 may be related to the 4 t ha^{-1} lime applied in 1972 to maintain soil pH at above 6. This pH increase would have led to greater sorption of Cd and hence a decrease in exchangeable Cd concentration, which is what was observed in sorption/desorption experiments in Chapter 4. Table 9.4 shows that although a significant proportion of newly added Cd ended up associated with the organic fraction, a substantial proportion of added Cd accumulated in the residual fraction of the soil, which has important implications for the long term phytoavailability of Cd in soils.

9.3.3 Effect of residence time on Cd distribution

An initial investigation into the effect of residence time on Cd availability in soil was carried out by determination of total Cd from soil samples that were taken in 1958 and from the same plot again in 1979, after a period of 21 years of no superphosphate application.

Results indicated that there was a time effect for both the 376R and 564R treatments, where there was a significant decrease ($p < 0.05$) in total Cd for samples taken in 1958 and in 1979 (Table 9.5). This reduction in Cd may be a function of leaching from the upper 75 mm of this irrigated stony soil (see section 9.3.4). Samples were also subjected to extraction with EDTA and sequential desorption by 0.01 M $Ca(NO_3)_2$. Results indicated (Table 9.5) that both EDTA extractable Cd and the fraction of Cd desorbable with 0.01 M $Ca(NO_3)_2$ significantly decreased ($p < 0.05$) with time.

Table 9.5 Mean and standard errors of Cd concentrations (μg Cd kg^{-1}) from soils sampled in 1958 and 1979 from 376R and 564R treatments

Treatment	376R				564R			
Year	1958		1979		1958		1979	
	mean	s.e	mean	s.e	mean	s.e	mean	s.e
Total Cd	77.7	1.9	64.7	2.0	130.2	14.6	74.4	2.0
0.04 M EDTA	58.7	1.2	42.6	2.0	90.1	7.0	55.9	2.0
0.01 M $Ca(NO_3)_2$	19.8	1.0	12.2	1.0	26.3	2.0	18.2	1.0

A further investigation of samples from 1958 and 1979 was undertaken, using chemical fractionation (as outlined in section 9.2.4.1.1), to determine if there had been any change in the distribution of Cd in the soil as a consequence of time.

The concentration of Cd in each fraction, expressed as a percentage of total Cd for the 376R and 564R treatments are shown in Fig 9.6. The pattern of Cd distribution on both treatments appear very similar, with the smallest concentration of Cd associated with the exchangeable fraction, while most of the Cd was associated with the organic and residual fractions. While the exchangeable and two oxide fractions appeared not to have significantly changed with time, there was an apparent decrease in Cd associated with the organic fractions with a corresponding increase in the residual fraction (Fig 9.6 a,b).

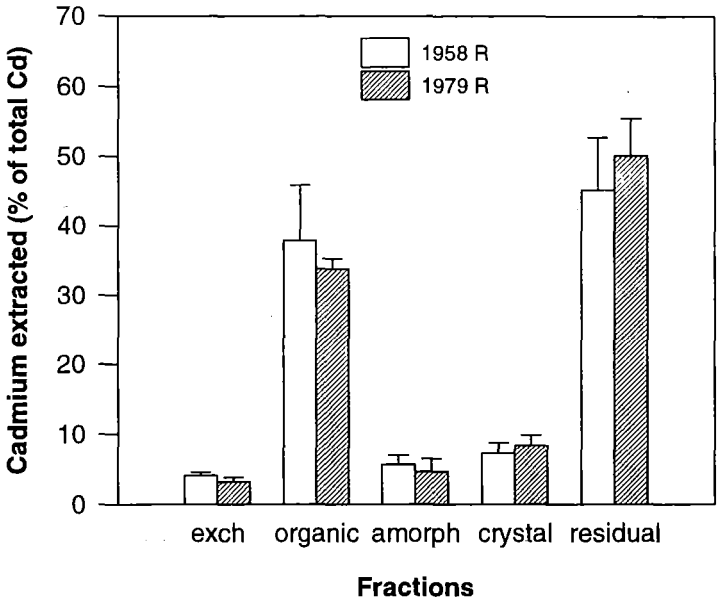


Fig 9.6a A comparison of the (%) of Cd in individual soil fractions for the 376R treatment for the years 1958 and 1979. Bars denote 95% CI.

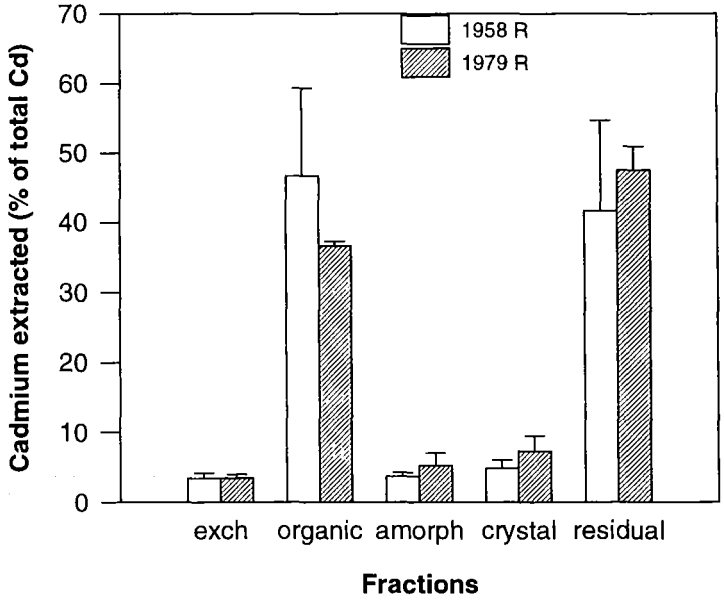


Fig. 9.6b A comparison of the (%) of Cd in individual soil fractions for the 564R treatment for the years 1958 and 1979. Bars denote 95% CI.

There was a decline in the more soluble fractions of Cd (organic) and an increase in the less available fractions (residual) during the 21 yr period of no superphosphate application. The results of the present study are similar to recent work reported by Hamon *et al.* (1997) who investigated immobilisation of Cd in soils. In this study, Cd phytoavailability was assessed for soil which had continuous superphosphate application, and soils in which superphosphate had been applied for a number of years and then application ceased (rundown plots). It was found that the percentage of non-phytoavailable Cd was higher on the rundown plots compared to the plots where superphosphate had been continuously applied. It was suggested that immobilisation of Cd had occurred on the rundown plots. Baerug and Singh (1990) compared Cd levels in soils and crops after long-term use of commercial fertilisers, found that Cd concentrations in plants from newly cultivated fields were higher than those on the old fertilised plots. While pH differences could explain part of the result, it seems that there was a decrease in the phytoavailable fraction of soil Cd as function of reaction time. Results in the present study along with evidence from other studies indicate that there is potential for Cd to become less phytoavailable with soil residence time.

9.3.4 Movement of soil Cd

Table 9.5 indicated that there was a decrease in soil Cd concentration with time, which may be linked to Cd movement out of the 75 mm sampling depth. As a result of these findings, samples were taken in 1995 at 50 mm intervals down to 150 mm, to further investigate movement of phytoavailable Cd in soil. Results indicate that in the superphosphate treated plots, there has been some downward movement of Cd, from its zone of application in the upper few mm, down the soil to depths of at least 150 mm (Table 9.6).

Table 9.6 Concentrations of Cd desorbed (5 desorptions μg Cd kg^{-1}) from soils taken at different soil depths in 1995 from Winchmore

	Treatment		
Depth (mm)	Control	188PA	376PA
0 - 50	8.8	34.7	40.4
50 - 100	8.1	27.8	38.2
100 - 150	8.0	23.0	32.2

Table 9.6 shows the cumulative desorption of Cd from the various depth samples in the superphosphate treated plots compared to the control. On the 376PA treatment, cumulative desorption significantly decreased ($p < 0.05$) from 40.4 μg Cd kg^{-1} in the 0 - 50 mm depth to 32.2 μg Cd kg^{-1} at 100 - 150 mm. On the 188PA treatment, cumulative desorption significantly decreased ($p < 0.05$) from 34.7 μg Cd kg^{-1} in the 0 - 50 mm depth to 23.0 μg Cd kg^{-1} at 100 - 150 mm. There was no significant change in the control.

The literature presents conflicting evidence about the importance of Cd losses through leaching. McGrath and Lane (1987) accounted for 80% of the Cd added to a soil through sewage sludge over a 20 year period. Similarly, Williams and David (1976) showed that approximately 80% of the Cd added to an arable soil via phosphate fertilisers was retained in the cultivated horizon, however for a sandy soil about 50% of the added Cd was lost from the upper part of the soil. Singh and Myhr (1997) investigated Cd leaching from Cd-enriched fertilisers in Norway and showed that Cd added in fertiliser did not move significantly through the soil. In contrast there have been other studies showing evidence of Cd movement (e.g. Dowdy *et al.* 1991). Rothbaum *et al.* (1986) found that only about 50% of the Cd added to a pasture soil was retained in the top 22.5 cm. Nicholson *et al.* (1995) constructed a Cd budget for a soil which had been under pasture for 80 years receiving regular additions of phosphate fertiliser and had been subject to atmospheric Cd deposition. Cadmium losses of between 2.4 - 4.9 g ha^{-1} yr^{-1} were calculated.

The mobility of Cd in soils depends on many soil and external factors. In general, at low metal concentration, sorption and desorption processes, (which control soil solution Cd concentrations) determine the amount of Cd available for leaching. The Winchmore soils are low in sorption components (i.e. Mn, Fe oxides, organic matter and clay) previously identified as important for sorption/desorption (Table 9.1). Furthermore, this soil is also subject to a flood irrigation regime (border dyke). These factors are likely to predispose this soil to leaching of added Cd. In addition, the effects of bioturbation, by earthworm activity may also have been important as a mechanism of Cd movement within the soil profile that can't be discounted.

9.4 Conclusions

This study investigated of the rate of Cd accumulation, its bioavailability, and distribution within the soil, from a trial that has received 44 years of superphosphate fertiliser application. Results indicated that there has been a significant accumulation of Cd in soil that has been subject to long term superphosphate fertiliser application. On the high fertiliser treatment 376PA, Cd was estimated to have accumulated at the rate of 7.8 g ha^{-1} yr^{-1}, which was similar to other studies. During the course of the trial, there was an increase in the proportion of Cd associated with exchangeable and organic soil fractions on the fertilised plots, which was related to a corresponding increase in soil organic carbon. Results also indicate that although there was a large proportion of added Cd associated with the organic fraction, the concentration of fertiliser applied Cd in the residual fraction was also substantial (i.e > 25% of added Cd). In addition, an investigation into the residence time of Cd in soil indicated that there was a redistribution of Cd into less soluble forms with time (i.e. residual Cd) along with a decrease in total soil Cd concentration. There was also evidence of movement of Cd down the soil profile in this irrigated soil. These results have implications for Cd phytoavailability with indicated decreased Cd availability with time.

Chapter 10

General discussion, main conclusions and future work

10.1 General discussion

In New Zealand, phosphate fertiliser application has been identified as the source of increased Cd concentrations in some pasture soils (Roberts *et al.* 1994). Elevated Cd concentrations in pasture soils have been shown to lead to enhanced Cd uptake by pasture. Sheep and other ruminants grazing this pasture can absorb a small, yet significant, proportion of this Cd, some of which is subsequently stored in the liver and kidneys of the animal. As a result, Cd in the offal of these animals could pose a threat to New Zealand's offal export trade, with Cd concentration used as a non-tariff trade barrier. In addition, the maximum permitted concentration (MPC) of Cd in foodstuffs in New Zealand is currently set at 1 mg kg^{-1} FW (with the exception of some shellfish), although this limit is currently under review with concentrations likely to be harmonised with Australia by 1999. The new limits will result in a lowering of the MPC for a number of important food products.

It is clear from the literature that little is known about soil Cd chemistry and plant uptake of Cd at concentrations in soil that are relevant to New Zealand agricultural conditions. The vast proportion of existing literature involves Cd concentrations that are often orders of magnitude higher than those encountered in New Zealand. Furthermore, previous studies have often used Cd added to soil as soluble inorganic salts or sewage sludge, which have been shown to behave differently to Cd added to soil in fertilisers. Therefore the main objective of the present study was to investigate the phytoavailability of Cd within a New Zealand environment and try to identify management strategies to minimise Cd uptake into plants.

The phytoavailability, and hence potential toxicity of Cd in soil, depends upon the concentration of Cd in soil solution and the ability of the solid phase to replenish Cd. The soil solution concentration of Cd in soil, especially low concentrations, is probably controlled, like other trace metals, by sorption/desorption phenomena at soil colloid surfaces (Swift and McLaren 1991). As a consequence, a study was carried out to

investigate sorption and desorption of both native and added Cd with the aim of examining the effect of soil pH on Cd sorption/desorption and to investigate the effect of Cd contact time on desorption.

Six soils with pHs ranging from pH 4.9 to pH 6.2 were selected for study. Results showed there was a large range in the concentration of Cd sorbed (38 to 96%) from an initial addition of 2 μg Cd g^{-1} in the soils studied. The effect of increasing soil pH resulted in a substantial increase in Cd sorption. This was thought to be predominantly a function of the dissociation of functional groups associated with organic matter, which was the dominant soil component in the soils studied. The importance of organic carbon with regard to sorption was confirmed by the finding that organic carbon and soil pH together accounted for 87% of Cd sorption. In contrast, the concentrations of both native and added Cd desorbed from the same soils decreased substantially with an increase in soil pH. Examination of desorption isotherms indicated that at lower pH, the larger concentrations of Cd desorbed with initial desorption events was Cd associated with low affinity sorption sites, while at higher pH values, the smaller concentrations of Cd desorbed indicated a greater number of stronger or high affinity sorption sites. In addition, there was also evidence to suggest that newly added Cd, added as $Cd(NO_3)_2$ salt, was not held as tightly as native soil Cd. This may indicate that newly added Cd interacts with different binding sites compared with the bulk of the initial Cd present in the soil.

Four soils, which differed in their Cd sorption/desorption capacity were selected for a study into the effects of contact time on desorption. An increase in contact time to 70 days before desorption between the soil and added Cd resulted in a subsequent reduction in desorption of Cd into solution. This varied between soil types, with the greatest effect related to the content of soil oxide components previously shown to sorb Cd irreversibly. There have been various mechanisms proposed for decreases in metal availability with time. These have included solid state diffusion of ions into mineral lattices structures, or possibly a redistribution of ions to more strongly bound or less accessible sorption sites involving diffusion into extremely small pores. A recent study by Fisher *et al.* (1996) has suggested the presence of wedge-shaped micropore structures at domain boundaries in goethite particles, which may affect desorption of sorbed metals. Given that the effects of

contact time in the present study occurred with 30 days or less, it appears plausible that there has been a redistribution of Cd to less available forms with time as a result of diffusion into extremely small pores.

The importance of soil pH and organic carbon as soil factors controlling sorption and desorption of Cd was clearly obvious using a small range of soil types. To further examine other soil properties controlling sorption and desorption of native and added soil Cd, along with Cd solubility, an investigation was carried out using a larger group of soils with a more diverse range of chemical and physical properties.

It was found that the solubility, sorption and desorption of native and added Cd varied greatly between the 29 soils studied. While correlation analysis again revealed that pH was the most dominant soil variable affecting solubility, sorption or desorption of native and added Cd, organic carbon, CEC and total soil Cd were also found to be important soil parameters.

The phytoavailability of Cd is dependent upon the concentration of Cd in soil solution, hence identification of soil factors which affect Cd solubility is extremely important with regard to understanding the behaviour of Cd in the soil system. Regression analysis revealed that Cd solubility was found to be controlled by soil pH, organic carbon, and total soil Cd concentration, with these parameters explaining 87% of the variability in Cd solubility. When the data in the present study was compared to data from a different study where Cd had added to soils in the form of sewage sludge, a single regression equation could be generated using the same 3 parameters (i.e. pH, organic carbon, total Cd). This reinforces the importance of these parameters in controlling Cd solubility in soils. In addition, the same 3 parameters were also shown to control native Cd desorption, which is an indication of the ability of the soil to replenish soil solution Cd concentrations.

Organic carbon and pH could also explain 75% of the variability in Cd sorption, while pH and CEC together could explain 77% of the variability of added Cd desorption. Interestingly, other soil components e.g. Fe, Al, and Mn oxides were not shown to be important with regard to sorption/desorption as in other studies. This may be a reflection

of the small amounts of these soil constituents in the soils studied, or possibly their effects were masked by organic coatings.

The fraction of potentially desorbable added Cd in soils could also be predicted from the sorption capacity of a soil (i.e. K_d value). This could be have potential value for assessing the mobility of Cd in soil and its likely phytoavailability. It is clear therefore from this study that a combination of soil properties control the solubility, sorption and/or desorption of Cd in soils.

As has already been implied, while there is an abundance of literature on Cd chemistry, there is a shortage of data relevant to the New Zealand soil environment. This extends to the identification of suitable soil extractants to predict plant uptake of Cd from soils, especially at low Cd concentrations. An evaluation of 8 commonly used soil extractants was undertaken, along with an investigation into Cd uptake by several vegetable, cereal and pasture species using soils where Cd was derived from either the soil parent material or from the application of phosphate fertiliser. The concentration of Cd extracted from the 10 soils studied varied greatly depending on the reagent used. For most soils however, the concentration of Cd extracted were in the order: 0.05 M AAAc-EDTA > 0.04 M EDTA > 1 M NH_4Cl > 0.05 M $CaCl_2$ > 1 M NH_4OAc > 0.05 M $Ca(NO_3)_2$ > 1 M NH_4NO_3 > 0.01 M $CaCl_2$. For most soil extractants, there was a positive relationship between the concentration of Cd extracted from the soil and the concentration of Cd in the plant. The correlation levels between plant Cd concentration and extractable soil Cd however varied depending upon the plant species and the extractant used. When all plants were analysed together, it was found that 0.05 M $Ca(NO_3)_2$ was the best predictor of plant Cd concentration. While the merits of various soil extractants as measure of Cd phytoavailability have been discussed, in the present study, it was found that a unbuffered or neutral extractant such as NH_4OAc, $CaCl_2$, or $Ca(NO_3)_2$ was regarded as a suitable predictor of plant Cd concentration.

Plant species vary greatly in their ability to absorb Cd from soils because of genetic differences. In general, when grown in the same soil, Cd accumulation by different plant species decreases in the order, leafy vegetables > root vegetables > grain crops. In this

study, plant cadmium concentrations varied greatly between different plant species, but generally followed the observed trends with greatest Cd uptake in lettuce and to a lesser extent carrot tops, and least barley. With the exception of lettuce, all plants were within the MRL for the Cd content of all foodstuffs intended for human consumption.

The results from the study investigating solubility, sorption and desorption of Cd identified soil pH as an important soil property controlling sorption/desorption and solubility of native and added soil Cd, and therefore likely to play a role in influencing Cd phytoavailability. Therefore a pot trial was set up to evaluate whether soil pH could be used in the management of plant Cd concentrations. The results indicated that in general, increasing soil pH from 5.5 to 7.0 was found to have a dramatic effect on reducing Cd concentrations in clover, lettuce, carrot and ryegrass, and to a lesser extent in wheat, although the magnitude of reduction varied between plant species and soil types. The decrease in plant Cd concentration as pH increases, was a result of the effect pH has on retention of Cd by soil surfaces. As soil pH increases, sorption of Cd onto soil components increases. There is also an concomitant decrease in desorption of Cd from these components into soil solution with increasing soil pH as shown in chapter 4. Therefore, increasing soil pH leads to a reduction of Cd in soil solution.

In addition, a re-evaluation of the soil extractants as predictors of plant Cd concentrations showed that extractants which were sensitive to soil pH and could extract moderate concentrations of Cd were found to be the most effective in predicting plant Cd concentration (e.g. 0.05 M $Ca(NO_3)_2$, 1 M NH_4OAc, 0.05 M $CaCl_2$ and 0.04 M EDTA).

A more detailed examination of soil Cd was undertaken by means of a fractionation scheme, which separated Cd into exchangeable, organic-bound, oxide-bound and residual fractions. A chemical fractionation technique was used to determine the forms and concentrations of native (or fertiliser derived) Cd in 12 New Zealand topsoils. The results showed there was a wide range in the concentrations of Cd associated individual soil fractions. The greatest concentration of Cd was associated with the organic and residual fractions, while the lowest concentration of Cd was in the exchangeable form. It seems that a substantial proportion of Cd added to the soil as a result of fertiliser application was

present in the residual fraction of the soils studied. These results suggest that a large proportion of native soil Cd in these soils is in forms likely to be in unavailable for plant uptake. There was also evidence to suggest that soil extractants that are commonly used to determine plant Cd concentrations (i.e. EDTA, AAAc-EDTA) include non-exchageable forms of Cd.

An important aspect of assessing Cd phytoavailability is evaluating changes in phytoavailability with time. An investigation of the rate of Cd accumulation, its bioavailability, and distribution within the soil, from a trial that has received 44 years of superphosphate fertiliser application was carried out. Results showed that there has been a significant accumulation of Cd in soil that has been subject to long term superphosphate fertiliser application. On the high fertiliser treatment, where superphosphate had been applied at the rate of 376 kg^{-1} ha^{-1} yr^{-1}, Cd was estimated to have accumulated at a rate of 7.8 g ha^{-1} yr^{-1}. A chemical fractionation of soil samples taken at regular intervals during the course of the trial, indicated that there has been an increase in the proportion of Cd associated with exchangeable and organic soil fractions on the fertilised plots, which was related to a corresponding increase in soil organic carbon. In the fertilised plots there was an increase in total carbon from 2.8% at the start of the trial, to 4.2% in 1996. This increase in organic carbon would have provided additional sorption sites for Cd added in to the soil. Whilst a significant proportion of the newly added Cd was associated with the organic fraction, there was still a substantial proportion bound up in the residual fraction, which has important implications for long-term Cd phytoavailability. In addition there was a redistribution of Cd into less soluble forms with time (i.e. residual Cd) along with a decrease in total soil Cd concentration on plots where superphosphate had been applied and then there was a hiatus before the same plots re-sampled. There was also evidence of movement of Cd down the soil profile in this irrigated soil.

10.2 Main conclusions

- Soil pH was found to be the most important soil property influencing Cd phytoavailability. Increasing soil pH was shown to result in significant decreases in the concentrations of native and added Cd desorbed from the soil, while there were significant increases in Cd sorption. Soil organic carbon was also an important soil

component controlling sorption and desorption of Cd. Soil pH along with organic carbon and total soil Cd concentrations were the soil properties found to be most important for controlling Cd solubility. In addition increasing soil pH was shown in a pot trial to significantly decrease plant Cd concentrations, in five different plant species.

- There was evidence of immobilisation of Cd in soils as a result of increased contact time between the soil and added Cd. Results from both an incubation study where Cd was added as a salt, and from a long-term superphosphate trial where Cd has been added to soil, fertiliser application ceased and the same soil re-sampled 21 years later, indicated that in both studies there was a decrease in the proportion of soluble Cd with time.

- Plant Cd concentrations varied greatly between different plant species. [illegible] plants were within the MRL for the Cd content of all foodstuffs intended for human consumption. In an evaluation of soil extractants that could predict plant Cd concentrations. It was found that a unbuffered or neutral extractant such as NH_4OAc, $CaCl_2$, or $Ca(NO_3)_2$ which was sensitive to soil pH was a suitable predictor of plant Cd.

- The long-term application of superphosphate fertiliser resulted in an accumulation of Cd on an irrigated pasture. On fertilised plots, there was an increase in Cd associated with the exchangeable and organic fractions with time, however there was still a substantial proportion of Cd in non-available residual forms. Similarly, for 12 topsoil samples in a separate study, while there was a wide range in the concentrations of Cd associated with individual soil fractions the greatest concentration of Cd was associated with the organic and residual fractions, with substantial proportions of Cd added as a result of fertiliser application was present in the residual fraction.

Revisiting the overall objectives of this study, which were to identify management strategies to control the phytoavailability of soil Cd, results indicate that several approaches may be employed. The maintenance of soil pH within a target range of 5.8-6.0 will not only increase sorption of Cd but will decrease desorption of Cd and reduce Cd solubility. Obviously organic carbon is involved in controlling solubility, sorption and desorption of

Cd in soil. The adoption of farming practices which maintain adequate organic matter levels in the soil should be encouraged. Total soil Cd concentrations were shown to be important with regard to plant Cd concentrations and was also a key variable in Cd solubility. The selection of P fertilisers with low Cd concentrations is to be promoted to reduce soil Cd concentrations. This has been made easier by a voluntary reduction policy for Cd contents of phosphate fertilisers adopted by the NZFMRA, which has set a maximum Cd concentration of 280 mg Cd kg^{-1} P. There is also some evidence to indicate that while Cd accumulation in soils as a consequence of P fertiliser application, it may become less plant available with time. As a management strategy, a 'hands off' approach may be suitable if this is indeed the case. In addition, a review of the literature has highlighted that there are a number of other possible strategies available to reduce Cd phytoavailability which should be considered.

10.3 Future research

Whilst the present study has improved in part our understanding of some of the chemistry of Cd at low concentrations in soils and its phytoavailability, the results have also raised a number of important questions and highlighted the need for further research into a number of key areas.

- There appears to no consensus on the mobility of Cd in soils. For example, in a recent study by Singh and Myhr (1997) investigating Cd leaching from Cd-enriched fertilisers in Norway, Cd added through fertilisers did not move significantly through the soil. However in the present study, there was evidence of movement of the desorbable fraction of Cd down the soil profile. Furthermore, Roberts and Longhurst (1997) have constructed and tested a preliminary Cd balance model. Results of measured and predicted Cd accumulation did not concur, pointing to a lack of reliable parameter values in some aspects of the model (e.g. leaching data). Therefore a leaching study is required to quantify the mobility of Cd added to different soils from fertiliser application.

- Another area which warrants investigation is the changes in the chemical forms of added Cd with length of contact with the soil. There was evidence in the present study from

both an incubation experiment and from a long-term field trial that the proportion of soluble Cd in soil decreases with contact time. Similarly, recent information from Australia (Hamon *et al.* 1997b) suggests that some 'fixation' of Cd in soils occurs. An investigation to study the immobilisation of Cd using radio-isotopic techniques, similar to those used in the study by (Hamon *et al.* 1997b) could be employed to further our knowledge in this area.

- In Europe, it has been recognised that there are significant atmospheric additions of Cd to soil. While this study has focused on fertiliser additions, there is a need to quantify the concentrations of Cd added to soils from atmospheric accession.

- While a pot experiment identified a number of soil extractants which could be successful predictors of plant Cd concentrations, a field based study is required to re-evaluate some of the soil extractants, as often results of laboratory or glasshouse experiments differ from field studies.

- A survey of Cd concentrations in a limited number of crops in Auckland and Canterbury by Roberts *et al.* (1995), revealed that Cd concentrations in wheat were close to the new MRL proposed by the ANZFA for this crop. Studies overseas have highlighted several strategies to minimise Cd uptake by wheat and a number of other crops which warrant investigation in New Zealand. The effect of Zn application to soils as a method of amelioration of Zn deficiency and as a way of reducing plant Cd concentrations in soils is worth examining. So too is the screening for plant cultivars which are low Cd accumulators. A field based study to investigating the effect of soil pH on plant Cd concentration is also worth consideration given the success of the pot experiment in the present study.

REFERENCES

Abdel-Sabour, M. F., Mortvedt, J. J., and Kelsoe, J. J. (1988). Cd-Zn interactions in plants and extractable Cd and Zn fractions in soil. *Soil Science* **145**, 424-431.

Ainsworth, C. C., Pilon, J. L., Gassman, P. L., and Van Der Sluys, W. G. (1994). Cobalt, cadmium, and lead sorption to hydrous iron oxide: Residence time effect. *Soil Science Society of America Journal* **58**, 1615-1623.

Alloway, B. J. (1986). Cadmium and lead in soils and vegetables: Investigation of the factors controlling concentrations in soil solutions and the tissues of crop plants. DoE Project PECD 7/8/05.

Alloway, B. J. (1990). Cadmium. *In* 'Heavy Metals in Soils'. (Ed B. J. Alloway) pp. 100-124. (Blackie: Glasgow.)

Alloway, B. J., and Steinnes, E. (1997). Anthropogenic additions of cadmium to soil: Review. *In* Proceedings of Fourth International Conference on the Biogeochemistry of Trace Metals pp. 663-664. San Francisco, 23 - 27 June 1997.

Alloway, B. J., Thornton, I., Smart, G. A., Sherlock, J., and Quinn, M. J. (1985). *Trace Substances in Environmental Health* **18**, 187-201.

Alloway, B. J., Jackson, A. P., and Morgan, H. (1990). Accumulation of cadmium by vegetables grown on soils contaminated from a variety of sources. *The Science of the Total Environment* **91**, 223-236.

Andersson, A. (1976). On the influence of manure and fertiliser on the distribution and amounts of plant available Cd in soils. *Swedish Journal of Agricultural Research* **6**, 19-25.

Andersson, A. (1977). Heavy metals in Swedish soils. On their retention, distribution and amounts. *Swedish Journal of Agricultural Research* **7**, 7-20.

Andersson, A., and Nilsson, K. O. (1974). Influence of lime and soil pH on cadmium availability to plants *Ambio* **3**, 198-200.

Andersson, A., and Siman, G. (1991). Levels of cadmium and some other trace elements in soils and crops as influenced by lime and fertiliser level. *Acta Agriculture Scandinavica* **41**, 3-11.

Andrewes, P., Town, R. M., Hedley, M. J., and Loganathan, P. (1996). Measurement of plant available cadmium in New Zealand soils. *Australian Journal of Soil Research* **34**, 441-452.

Auer, C. (1977). Cadmium in phosphate fertiliser production. US EPA Midwest Research Instruction Report, October 1977. (United States Environmental Protection Agency: Cincinnatti, OH, USA.)

Backes, C. A., McLaren, R. G., Rate, A. W., and Swift, R. G. (1995). Kinetics of cadmium and cobalt desorption from iron and manganese oxides. *Soil Science Society of America Journal* **59**, 778-785.

Baerug, R., and Singh, B. R. (1990). Cadmium levels in soils and crops after long-term use of commercial fertilizers. *Norwegian Journal of Agricultural Sciences* **44**, 251-260.

Bailey, V. L., Grant, C. A., Racz, G. J., and Bailey, L. D. (1995). A practical method for assessing cadmium levels in soil using the DTPA extraction technique with graphite furnace analysis. *Communications in Soil Science and Plant Analysis* **26,** 961-968.

Bajracharya, K., Tran, Y. T., and Barry, D. A. (1996). Cadmium adsorption at different pore water velocities. *Geoderma* **73**, 197-216.

Barrow, N. J. (1984). Modelling the effects of pH on phosphate adsorption by soils. *Journal of Soil Science* **35**, 283-297.

Barrow, N. J. (1986). Testing a mechanistic model. IV. Describing the effect of pH on Zn retention by soils. *Journal of Soil Science* **37**, 295-302.

Beckett, P. H. T. (1989). The use of extractants in studies on trace metals in soils, sewage sludges and sludge-treated soils. *Advances in Soil Science* **9**,143-176.

Bell, M. J., McLaughlin, M. J.,Wright, G. C., and Cruickshank, A. (1997). Inter- and intra-specific variation in accumulation of cadmium by peanut, soybean, and navybean. *Australian Journal of Experimental Agriculture* **48**, 1151-1160.

Bell, P. F., James, B. R., and Chaney, R. L. (1991). Heavy metal extractability in long-term sewage sludge and metal salt-amended soils. *Journal of Environmental Quality* **20**, 481-486.

Benjamin, M. M., and Leckie, J. O. (1982). Effects of complexation by Cl, SO_4, and S_2O_3 on adsorption behaviour of Cd on oxide surfaces. *Environment Science and Technology* **16**, 162-170.

Berti, W. R., and Jacobs, L. W. (1996). Chemistry and phytotoxicity of soil trace elements from repeated sludge applications. *Journal of Environmental Quality* **25**, 1025-1032.

Bidwell, A. M., and Dowdy, R. H. (1987). Cadmium and zinc availability to corn following termination of sewage sludge applications. *Journal Environmental Quality* **16**, 438-442.

Bingham, F. T. (1979). Bioavailability of Cd to food crops in relation to heavy metal content of sludge-amended soil. *Environmental Health Perspective* **28**, 39-43.

Bingham, F. T., Page., A. L., Mahler, R. J., and Ganje, T. J. (1975). Growth and cadmium accumulation of plants grown on soil treated with a cadmium-enriched sewage sludge. *Journal Environmental Quality* **4** 207-211.

Bingham, F. T., Page., A. L., Mahler, R. J., and Ganje, T. J. (1976). Cadmium availability to rice in sludge-amended soil under 'flood' and 'nonflood' culture. *Soil Science Society of America Journal* **40**, 715-719.

Bingham, F. T., Sposito, G., and Strong, J. E. (1986). The effect of sulphate on the availability of cadmium. *Soil Science* **141**, 172-177.

Bittell, J. F., and Miller, R. J. (1974). Lead, cadmium and calcium selectivity coefficients on montmorillonite, illite and kaolinite. *Journal of Environmental Quality* **12**, 250-253.

Blakemore, L. C., Searle, P. L., and Daly, B. K. (1987). Methods for chemical analysis of soils. New Zealand Bureau Scientific Rep. 80. NZ. Soil Bureau, Lower Hutt, New Zealand.

Boekhold, A. E., and Van der Zee, S. E. A. T. M. (1991). Long-term effects of soil heterogeneity on cadmium behaviour in soil. *Journal of Contamination Hydrology* **7**, 371-390.

Boekhold, A. E., and Van der Zee, S. E. A. T. M. (1992). Significance of soil chemical heterogeneity for spatial behaviour of cadmium in field soils. *Soil Science Society of America Journal* **56**, 747-754.

Boekhold, A. E., Temminghoff, E. J. M., and Van der Zee, S. E. A. T. M. (1993). Influence of electrolyte composition and pH on cadmium sorption by an acid sandy soil. *Journal of Soil Science* **44**, 85-96.

Boggess, S. F., Willavize, S., and Koeppe, D. E. (1978). Differential response of soybean varieties to soil cadmium. *Agronomy Journal* **70**, 756-760.

Bowen, H. J. M. (1979). 'Environmental chemistry of the elements'. (Academic Press, London.)

Bramley, R. G. V. (1990). Cadmium in New Zealand agriculture. *New Zealand Journal Agricultural Research* **33**, 505-519.

Brams, E., and Anthony, W. (1988). Residual cadmium in a soil profile and accumulation in wheat grain. *Plant and Soil* **109**, 3-8.

Brown, S. L., Chaney, R. L., Lloyd, C. A., Angle, J. S., and Ryan, J. A. (1996). Relative uptake of cadmium by garden vegetables and fruits grown on long-term biosolid-amended soils. *Environmental Science and Technology* **30**, 3508-3511.

Bruemmer, G. W., Gerth, J., and Tiller, K. G. (1988). Retention kinetics of the adsorption and desorption of nickel, zinc and cadmium by goethite. I. Adsorption and diffusion of metals. *Journal of Soil Science* **39**, 37-52.

Buchter, B., Davidoff, B., Amacher, M. C., Hinz, C., Iskandar, I. K., and Selim, H. M. (1989). Correlation of Freundich K_d and retention parameters with soils and elements. *Soil Science* **148**, 307-379.

Cakmak, I., Gulut, K. Y., Marschner, H., Graham, R. D. (1994). Effect of zinc and iron deficiency on phytosiderophore release in wheat genotypes differing in zinc deficiency. *Journal of Plant Nutrition* **17**, 1-17.

Cameron, K. C., Di, H. J., and McLaren, R. G. (1997). Is soil an appropriate dumping ground for our wastes? *Australian Journal of Soil Research* **35**, 995-1035.

Cavallaro, N., and McBride, M. B. (1978). Copper and cadmium sorption characteristics of selected acid and calcareous soils. *Soil Science Society of America Journal* **42**, 550-556.

Cavallaro, N., and McBride, M. B. (1984). Zinc and copper sorption and fixation by an acid soil clay: effect of selective dissolutions. *Soil Science Society of America Journal* **48**, 1050-1054.

Chaney, R. L., and Hornick, S. B. (1978). Accumulation and effects of cadmium on crops. *In* Proc. 1st International Cadmium Conference, Metals Bulletin, Ltd., London p 125-140.

Chaney, R. L., Li, Y.-M., Schneiter, A. A., Green, G. E., and Hopkins, D. G. (1993). Progress in developing technologies to produce low Cd concentrations sunflower kernels. 'Proceedings 1993 Sunflower Research Forum, Jan. 14-15, 1993; Fargo, N.D.' (National Sunflower Association: Bismarck, N.D, USA.).

Chang, A. C., Page, A. L., Foster, K. W., and Jones, T. E. (1982). A comparison of cadmium and zinc accumulation by four cultivars of barley grown in sludge-amended soils. *Journal of Environmental Quality* **11**, 409-412.

Chang, A. C., Page, A. L., and Warneke, J. E. (1987). Long-term sludge application on cadmium and zinc accumulation in swiss chard and radish. *Journal of Environmental Quality* **16**, 217-221.

Chang, A. C., Page, A. L., Warneke, J. E., and Grgurevic, E. (1984). Sequential extraction of soil heavy metals following a sludge application. *Journal of Environmental Quality* **13**, 33-38.

Chang, A. C., Page, A. L., Waraeke, J. E., Resketo, M. R., and Jones, T. E. (1983). Accumulation of cadmium and zinc in barley grown on sludge-treated soil. *Journal of Environmental Quality* **12**, 391-397.

Chao, T. T. (1972). Selective dissolution of manganese oxides from soils and sediments with acidified hydroxylamine hydrochloride. *Soil Science Society of America Proceedings* **36**, 764-768.

Chardon, W. J. (1984). *Mobility of cadmium in soil* (in Dutch). Thesis, Ph.D., Agricultural University, Wageningen.

Choudhary, M., Bailey, L. D., and Grant, C. A. (1994). Effects of zinc on cadmium concentrations in the tissue of durum wheat. *Canadian Journal of Plant Science* **74**, 549-552.

Christensen T. H. (1984a). Cadmium soil sorption at low concentrations: I. Effect of time, cadmium load, pH, and calcium. *Water, Air, and Soil Pollution* **21**, 105-114.

Christensen, T. H. (1984b). Cadmium soil sorption at low concentrations: II. Reversibility, effect of changes in solute composition, and effect of soil aging. *Water, Air, and Soil Pollution* **21**, 115-25.

Christensen, T. H. (1987). Cadmium soil sorption at low concentrations: Evidence of competition by other heavy metals. *Water, Air, and Soil Pollution* **34**, 293-303.

Christensen, T. H. (1989). Cadmium soil sorption at low concentrations: VIII. Correlation with soil parameters. *Water, Air, and Soil Pollution* **44**, 71-82.

Chubin, R. G., and Street, J. J. (1981). Adsorption of cadmium on soil constituents in the presence of complexing ligands. *Journal of Environmental Quality* **10**, 225-228.

Chumbley, C. J., and Unwin, R. J. (1982). Cadmium and lead content of vegetable crops grown on land with a history of sewage sludge application. *Environmental Pollution* **4B**, 231-237.

Cieslinski, G., Neilsen, G. H., and Hogue, E. J. (1996). Effect of soil cadmium application and pH on growth and cadmium accumulation in roots, leaves and fruit of strawberry plants (*Fragaria* x *ananassa* Duch.). *Plant and Soil* **180**, 267-276.

Clayton, P. M., and Tiller, K. G. (1979). A chemical method for the determination of heavy metal content of soils in environmental studies. CSIRO Australia Division of Soils Technical Pater no. **41**.

Comans, R. N. J. (1987). Adsorption, desorption and isotopic exchange of cadmium on illite: Evidence for complete reversibility. *Water Resources* **21**, 1573-1576.

Cotton, F. A., and Wilkinson, G. (1966). 'Advanced inorganic chemistry'. (A comprehensive text. 2nd Ed. John Wiley, New York.)

David, D. J., Pinkerton, A., and Williams, C. H. (1978). Impurities in Australian phosphate fertilizers. *Journal of the Australian Institute of Agricultural Science* **44**, 132-135.

Day, P. R. (1965). Particle fractionation and particle size analysis, pp 545-67. *In*: C.A. Black (ed.) *Methods of Soil Analysis, Part 1.* Agronomy Monograph No. 9. American Society of Agronomy, Madison, WI.

De Boo, W. (1978). Cadmium in agriculture. *Toxicological and Environmental Chemistry* **27**, 55-63.

De Pieri, L. A., Buckley, W. T., and Kowalenko, C. G. (1997). Cadmium and lead concentrations of commercially grown vegetables and soils in the Lower Fraser Valley of British Columbia. *Canadian Journal of Soil Science* **77**, 51-57.

De Vries, M. P. C., and Tiller, K. G. (1978). Sewage sludge as a soil amendment with special reference to Cd, Cu, Mn, Ni, Pb, and Zn - comparison of results from experiments conducted inside and outside a glasshouse. *Environmental Pollution* **16**, 231-240.

Del Castilho, P., and Chardon, W. J. (1995). Uptake of soil cadmium by three field crops and its prediction by a pH-dependent Freundlich sorption model. *Plant and Soil* **171**, 263-266.

Delschen, T., and Werner, W. (1989). Zur Aussagekraft der Schwermetallgrenzwerte in klarschlammgedungten Boden. 2. Mitteilung: Beitrag zur Ableitung 'tolerierbaren' 0.1 M $CaCl_2$ -loslicher Cadmium und Zinkgehalte. *Landwirtsch. Forschung* **42** 41-49.

Doner, H. E. (1978). Chloride as a factor in mobilities of Ni(II), Cu(II) and Cd(II) in soil. *Soil Science Society of America Journal* **42**, 882-885.

Dowdy, R. H., Latterell, J. J., Hinesly, T. D., Grossman, R. B., and Sullivan, D. L. (1991). Trace metal movement in an aeric ochraqualf following 14 years of annual sludge applications. *Journal of Environmental Quality* **20**, 119-123.

Dudas, M. J. (1974). The quantitative determination of cadmium in soils by solvent extraction and flameless atomic spectroscopy. *Atomic Absorption Newsletter* **13**, 109-112.

Elliott, H. A., and Denneny, C. M. (1982). Soil adsorption of cadmium from solutions containing organic ligands. *Journal of Environmental Quality* **11**, 658-662.

Elliott, H. A., Liberali, M. R., and Huang, C. P. (1986). Competitive adsorption of heavy metals by soils. *Journal of Environmental Quality* **15**, 215-219.

Emmerich, W. E., Lund, L. J., Page, A. L., and Chang, A. C. (1982). Solid phase forms of heavy metals in sewage sludge-treated soils. *Journal of Environmental Quality* **11**, 178-181.

Eriksson, J. E. (1989). The influence of pH, soil type and time on adsorption and uptake by plants of Cd added to soil. *Water, Air, and Soil Pollution* **48**, 317-335.

Eriksson, J. E. (1990). Effects of nitrogen-containing fertilisers on solubility and plant uptake of cadmium. *Water, Air, and Soil Pollution* **49**, 355-368.

Farrah, H., and Pickering, W. F. (1977). Influence of clay-solute interactions on aqueous heavy metal ion levels. *Water, Air, and Soil Pollution* **8**, 189-197.

Fischer, L., Zur Muhlen, E., Bruemmer, G. W., and Niehus, H. (1996). Atomic force microscopy (AFM) investigations of the surface topography of a multidomain porous goethite. *European Journal of Soil Science* **47**, 329-334.

Forstner, U. (1980). Cadmium. *In* 'The handbook of environmental chemistry' Vol. 3. Part A anthropogenic compounds, (Eds O, Hutzinger). (Springer-Verlag, New York.)

Frank, R., Ishida, K., Suda, P. (1976). Metals in agricultural soils of Ontario. *Canadian Journal of Soil Science* **56**, 181-196.

Friberg, L. (1948). Proteinuria and emphysema among workers exposed to cadmium and nickel dust in a storage battery plant. Proceedings International Cong Ind Med 9, 641-644.

Garcia-Miragaya, J. (1980). Specific sorption of trace amounts of cadmium by soils. *Communications in Soil Science and Plant Analysis* **11**, 1157-1166.

Garcia-Miragaya, J., and Page, A. L. (1976). Influence of ionic strength and inorganic complex formation on sorption of trace amounts of cadmium by montmorillonite. *Soil Science Society of America Journal* **40**, 658-663.

Garcia-Miragaya, J., and Page, A. L. (1978). Sorption of trace quantities of cadmium by soils with different chemical and mineralogical composition. *Water, Air, and Soil Pollution* **9**, 289-299.

Garcia-Miragaya, J., Cardenas, R., and Page, A. L. (1986). Surface loading effect on Cd and Zn sorption by kaolinite and montmorillonite from low concentration solutions. *Water, Air, and Soil Pollution* **27**, 181-190.

Gerritse, R. G., and van Driel, W. (1984). The relationship between adsorption of trace metals, organic matter and pH in temperate soils. *Journal of Environmental Quality* **13**, 197-204.

Gerritse, R. G., Vriesma, R., Calenbery, J. W., and De Roos, H. P. (1982). Effect of sewage sludge on trace element mobility in soils. *Journal of Envirnonmental Quality* **11**, 359-364.

Ghoshesh, A., Bashir, S., and Dabbas, L. (1996). Managing the cadmium content of phosphate rock: A contribution to environmental impact mitigation. *In* Fertilizers as a source of cadmium. OECD proceedings. pp 13-20.

Gibson, M. J., and Farmer, J. G. (1986). Multi-step sequential chemical extraction of heavy metals from urban soils. *Environmental Pollution* **11**, 117-135.

Giles, C. H., D'Silva, A. P., and Easton, I. A. (1974). A general treatment and classification of the solute adsorption isotherm. Part II. Experimental interpretation. *Journal of Colloid and Interface Science* **47**, 766-778.

Giordano, P. M., Mays, D. A., and Behel, A. D. (1979). Soil temperature effects on uptake of cadmium and zinc by vegetables grown on sludge-amended soil. *Journal of Environmental Quality* **8**, 233-236.

Goering, P. L., Waalkes, M. P., and Klaassen, C. D. (1995). Toxicology of metals: Biochemical Aspects. (Eds Goyer, R.A., and Cherian, M.G).

Grant, C. A., and Bailey, L. D. (1997). Effects of phosphorus and zinc fertiliser management on cadmium accumulation in flaxseed. *Journal of the Science of Food and Agriculture* **73**, 307-314.

Grant, C., A., Bailey, L. D., and Therrien, M. C. (1996). Effect of N, P, and KCl fertilisers on grain yield and Cd concentration of malting barley. *Fertiliser Research* **45**, 153-161.

Gray, C. W., McLaren, R. G., Roberts, A. H. C., and Condron, L. M. (1998). Sorption and desorption of cadmium from some New Zealand soils: effect of pH and contact time. *Australian Journal of Soil Research* **36**, 199-216.

Guttormsen, G. (1990). Cadmium and lead levels in Norwegian vegetables. *Norwegian Journal of Agricultural Sciences* **4**, 95-101.

Guttormsen, G., Singh, B. R., and Jeng, A. S. (1995). Cadmium concentration in vegetable crops grown in a sandy soil as affected by Cd levels in fertiliser and soil pH. *Fertiliser Research* **41**, 27-32.

Haeni, H., and Gupta, S. (1983). Total and biorelevant heavy metal contents and their usefulness in establishing limiting values in soils. *In* 'Environmental Effects of Organic and Inorganic Contaminants in Sewage Sludge'. (Eds. R.D. Davis, G. Hucker and P. L'Hermite.) pp 121-129. (Reidel, Dordrecht, The Netherlands.)

Haghiri, F. (1974). Plant uptake of cadmium as influenced by cation exchange capacity, organic matter, zinc, and soil temperature. *Journal of Environmental Quality* **3**, 180-183.

Hamon, R., Wundke, J., McLaughlin, M., and Naidu, R. (1997). Availability of zinc and cadmium to different plant species. *Australian Journal of Soil Research* **35**, 1267-1277.

Han, D. H., and Lee, J. H. (1996). Effects of liming on uptake of lead and cadmium by *Raphanus sativa*. *Archives of Environmental Contamination and Toxicology* **31**, 488-493.

Hamon, R. E., McLaughlin, M. J., and Naidu, R. (1997b). Evidence for the immobilisation of cadmium in soils. *In* Proceedings of Fourth International Conference on the Biogeochemistry of Trace Metals pp. 425-426. San Francisco, 23 - 27 June 1997.

Haq, A. U., Bates, T. E., and Soon, Y. K. (1980). Comparison of extractants for plant-available zinc, cadmium, nickel and copper in contaminated soils. *Soil Science Society of America Journal* **44**, 772-777.

Harrison, H. C. (1986). Response of lettuce cultivars to sludge-amended soils and bed types. *Communications in Soil Science and Plant Analysis* **17**, 159-172.

He, Q. B., and Singh, B. R. (1993a). Plant availability of cadmium in soils. I. Extractable cadmium in newly and long-term cultivated soils. *Acta Agriculture Scandinavica* **43**, 134-141.

He, Q. B., and Singh, B. R. (1993b). Effect of organic matter on the distribution, extractability and uptake of cadmium in soils. *Journal of Soil Science* **44**, 641-650.

He, Q. B., and Singh, B. R. (1994). Cadmium uptake by crops from phosphorus fertilisers I. Yield and cadmium concentration. *Water, Air, and Soil Pollution* **74**, 251-265.

Helmke, P. A., and Naidu, R. (1996). 'Contaminants and the soil environment in the Australasia-Pacific Region'. Proceedings of the first Australasia-Pacific Conference on Contaminants and soil environment in the Australasia-Pacific Region, held in Adelaide, Australia, 18-23 Feburary 1996.

Hemphill, D. D., Jr, Jackson, T. L., Martin, L. W., Kiemnec, G. L., Hanson, D., and Volk, V. V. (1982). Sweetcorn response to application of three sewage sludges. *Journal of Environmental Quality* **11**, 191-196.

Hendrickson, L. L., and Corey, R. B. (1981). Effect of equilibrium metal concentrations on apparent selectivity coefficients of soil complexes. *Soil Science* **131**, 163-171.

Hewitt, A. E. (1993). 'New Zealand Soil Classification' Landcare Research Science Series No. 1 (Landcare Research: Lincoln, New Zealand).

Hickey, M. G., and Kittrick, J. A. (1984). Chemical partitioning of cadmium, copper, nickel, and zinc in soils and sediments containing high levels of heavy metals. *Journal of Environmental Quality* **13**, 372-376.

Hinesly, T. D., Alexander, D. E., Ziegler, E. L., and Barrett, G. L. (1978). Zinc and cadmium accumulation by corn inbreds grown on sludge-amended soil. *Agronomy Journal* **70**, 425-428.

Hodgson, J. F., Tiller, K. G., and Fellows, M. (1964). The role of hydrolysis in the reaction of heavy metals with soil-forming materials. *Soil Science Society of America Proceedings* **28**, 42-46.

Hogg, D. S., McLaren, R. G., and Swift, R. S. (1993). Desorption of copper from some New Zealand soils. *Soil Science Society of America Journal* **57**, 361-366.

Hoins, U., Charlet, L., and Sticher, H. (1993). Ligand effect on the adsorption of heavy metals: The sulfate-cadmium-goethite case. *Water, Air and Soil Pollution* **68**, 241-255.

Holm, P. E., Futtrup, J., Christensen, T. H., and Tjell, J. C. (1993). Determination of cadmium species in soil solution samples. In 'Heavy Metals in the Environment. Volume 1'. (Eds R. J. Allen and J. O Nriagu.) pp. 290-293.

Holmgren, G. G. S., Meyer, M. W., Chaney, R. L., Daniels, R. B. (1993). Cadmium, lead, zinc, copper, and nickel in agricultural soils of the United States of America. *Journal of Environmental Quality* **22**, 335-348.

Homann, P. S., and Zasoski, R. L. (1987). Solution composition effects on cadmium sorption by forest soil profiles. *Journal of Environmental Quality* **6**, 429-433.

Honman, Y., and Hirata, H. (1978). A noticeable increase in Cd absorption by Zn deficient rice plants. *Soil Science and Plant Nutrition* **24**, 295-297.

Hooda, P. S., and Alloway, B. J. (1993). Effects of time and temperature on the bioavailability of Cd and Pb from sludge-amended soils. *Journal of Soil Sci*ence **44**, 97-110.

Hooda, P. S., and Alloway, B. J. (1994). Sorption of Cd and Pb by selected temperate and semi-arid soils: effects of sludge application and ageing of sludged soils. *Water, Air and Soil Pollution* **74**, 235-250.

Hooda, P. S., and Alloway, B. J. (1997). The effect of liming on heavy metal concentrations in wheat, carrots and spinach grown on previously sludge-applied soils. *Journal of Agricultural Science*, Cambridge **127**, 289-294.

Hooda, P. S., McNulty, D., Alloway, B. J., and Aitken, M. N. (1997). Plant availability of metals in soils previously amended with heavy metal applications of sewage sludge. *Journal of Science and Food Agriculture* **73**, 446 -454.

Hovmand, M. F. (1981). Cirkulation af bly, cadmium, kobber, zink og nickl I dansk landburg. In 'Slammets Jordbrugsandvendels, Vol. II Fokusering'. Pp. 85-118. (Polyteknisk Forlag: Lyngby.).

Hovmand, M. F., Tjell, J. C., and Mosbaek, H. (1983). Plant uptake of airborne cadmium. *Environmental Pollution (Series A)* **30**, 27-38.

Hutton, M., and Symon, C. J. (1986). The quantities of cadmium, lead, mercury and arsenic entering the U.K. environment from human activities. *Science of the Total Environment* **57**, 129-150.

Inskeeps, W. P., and Baham, J. (1983). Adsorption of Cd(II) and Cu(II) by Na-montmorillonite at low surface coverage. *Soil Science Society of America Journal* **47**, 660-665.

Isermann, K. (1982). Effect of phosphate fertilization on the cadmium content of soil determined on the basis of numerous long-term trials in Western Europe. Landwirtschaft. *Forsch. Sonderheft* **39**, 283-301.

Jaakola, A. (1977). Effects of fertilisers, lime and cadmium added to soil on the cadmium content of spring wheat. *Journal Science Agricultural Society Finland* **49**, 406-414.

Jackson, A. P., and Alloway, B. J. (1991). The phytoavailability of cadmium to lettuces and cabbages in soils previously treated with sewage sludges. *Plant and Soil* **132**, 179-186.

Jarvis, S. C., and Jones, L. H. P. (1980). The contents and sorption of cadmium in some agricultural soils of England and Wales. *Journal of Soil Science* **31**, 469-479.

Jensen, H., and Mosbaek, H. (1990). Relative availability of 200 years old cadmium from soil to lettuce. *Chemosphere* **20**, 693-702.

Jinadasa, K. B. P. N., Milham, P. J., Hawkins, C. A., Cornish, P. S., Williams, P. A., Kaldor, C. J., and Conroy, J. P. (1997). Survey of cadmium levels in vegetables and soils of greater Sydney, Australia. *Journal of Environmental Quality* **26**, 924-933.

Jing, J., and Logan, T. J. (1992). Effect of sewage sludge cadmium concentration on chemical extractability and plant uptake. *Journal of Environmental Quality* **21**, 73-81.

John, M. K. (1972). Effect of lime on soil extraction and on the availability of soil applied cadmium to radish and leaf lettuce plants. *Science of the Total Environ*ment **1**, 303-308.

John, M. K., Van Laerhoven, C. J., and Chuah, H. H. (1972). Factors affecting plant uptake and phytoxicity of Cd added to soils. *Environmental Science and Technology* **67**, 1005-1019.

Johnston, A. E., and Jones, K. C. (1995). The origin and fate of cadmium in soil. Proceedings of Fertiliser-Society, No. 366, 39 pp.

Jones, K. C., Symon, C. J., and Johnston, A. E. (1987). Retrospective analysis of an archived soil collection. II. Cadmium. *Science of the Total Environment* **67**, 75-89.

Kabata-Pendias, A., and Pendias, H. (1992). 'Trace Elements in Soils and Plants.' (CRC Press: Baton Raton, FL, USA.).

Keller, C., and Vedy, J. C. (1994). Distribution of copper and cadmium fractions in two forest soils. *Journal of Environmental Quality* **23**, 987-999.

Kim, N. D., and Fergusson, J. E. (1992). Adsorption of cadmium by an Aquent New Zealand soil and its components. *Australian Journal of Soil Research* **30**, 159-167.

King, L. D. (1988). Retention of cadmium by several soils of Southeastern United States. *Journal of Environmental Quality* **17**, 246-250.

Kofoed, A. M., and Klausen, D. S. (1983). Influence of fertiliser on the cadmium content of soils and crops. *Tidsskr. Planteavl.* **87**, 23-32.

Kookana, R. S., Naidu, R., and Tiller, K. G. (1994). Sorption non-equilibrium during cadmium transport through soils. *Australian Journal of Soil Research* **32**, 635-651.

Kookana, R. S., Naidu, R., and Tiller, K. G. (1997). Desorption of cadmium is determined by its adsorption affinity to soils. In Proceedings of Fourth International Conference on the Biogeochemistry of Trace Metals pp 399-400. San Francisco, 23-27 June 1997.

Krishnamuriti, G. S. R., Huang, P. M., Van Rees, K. C. J., Kozak, L. M., and Rostad, H. P. W. (1994). Microwave digestion techniques for the determination of total cadmium in soils. *Communications in Soil Science and Plant Analysis* **25**, 615-625.

Krishnamuriti, G. S. R., Huang, P. M., Van Rees, K. C. J., Kozak, L. M., and Rostad, H. P. W. (1995a). Speciation of particulate-bound cadmium of soils and its bioavailability. *Analyst* **120**, 659-665.

Krishnamuriti, G. S. R., Huang, P. M., Van Rees, K. C. J., Kozak, L. M., and Rostad, H. P. W. (1995b). A new soil test method for the determination of plant-available cadmium in soils. *Communications in Soil Science and Plant Analysis* **26**, 2857-2867.

Kuo, S. (1990). Cadmium buffering capacity and accumulation in Swiss Chard in some sludge-amended soils. *Soil Science Society of America Journal* **54**, 86-91.

Kuo, S., and Baker, A. S. (1980). Sorption of copper, zinc and cadmium by some acid soils. *Soil Science Society of America Journal* **44**, 969-974.

Kuo, S., and McNeal, B. L. (1984). Effects of pH and phosphate on cadmium sorption by a hydrous ferric oxide. *Soil Science Society of America Journal* **48**, 1040-1044.

Kuo, S., and Mikkelsen, D. S (1980). Kinetics of zinc desorption from soils. *Plant and Soil* **56**, 355-364.

Lagerweff, J. V. (1971). Uptake of cadmium, lead and zinc by radish from soil and air. *Soil Science* **111**, 129-133.

Lagerwerff, J.V. (1972). Cadmium. *In* 'Micronutrients in agriculture'. (Eds Mortvedt, J. J., Giordano, P. M., Lindsay, W. L.). pp. 619-639 (Soil Science Society of America Incorporated, Madison, Wisconsin, USA.)

Lakanen, E., and Ervio, R. (1971). A comparison of eight extractants for the determination of plant available micronutrients in soils. *Acta Agral. Fenn.* **123**, 223-232.

Lake, D. L., Kirk, P., and Lester, J. (1984). Fractionation, characterization, and speciation of heavy metals in sewage sludge and sludge-amended soils: A review. *Journal of Environmental Quality* **13**, 175-183.

Lee, D. Y., and Zheng, H. C. (1993). Chelating resin membrane method for estimation of soil cadmium phytoavailability. *Communications in Soil Science and Plant Analysis* **24**, 685-700.

Lee, J., Rounce, J. R., Mackay, A. D., Grace, N. D. (1996a). Accumulation of cadmium with time in Romney sheep grazing ryegrass-white clover pasture: effect of cadmium from pasture and soil intact. *Australian Journal of Agricultural Research* **47**, 887-894.

Lee, S. Z., Allen, H. E., Huang, C. P., Sparks, D. L., Sanders, P. F., and Peijnenburg, W. J. G. M. (1996b). Predicting soil-water partition coefficients for cadmium. *Environmental Science and Technology* **30**, 3418-3424.

Lehmann, R. G., and Harter, R. D. (1984). Assessment of copper-soil bond strength by desorption kinetics. *Soil Science Society of America Journal* **48**, 769-772.

Levi-Minzi, R., Soldatini, G. F., and Riffaldi, R. (1976). Cadmium adsorption by soils. *Journal of Soil Science* **27**, 10-15.

Li, Y.-M., Chaney, R. L., and Schneiter, A. A. (1994). Effect of soil chloride level on cadmium concentration in sunflower kernels. *Plant and Soil* **167**, 275-280.

Li, Y.-M., Chaney, R. L., Schneiter, A. A., and Johnston, B. L. (1996). Effect of field limestone applications on cadmium content of sunflower (*Helianthus annuus* L.) leaves and kernels. *Plant and Soil* **180**, 297-302.

Li, Y. M., Chaney, R. L., Schneiter, A. A., and Miller, J. F. (1995). Genotypic variation in kernel cadmium concentration in sunflower germplasm under varying soil conditions. *Crop Science* **35**, 137-141.

Lindsay, W. L (1979). 'Chemical Equilibria in Soils.' (John Wiley: New York.)

Lindsay, W. L., and Norvell, W. A. (1978). Development of a DTPA soil test for zinc, iron, manganese and copper. *Soil Science Society of America Journal* **42**, 421-428.

Loganathan, P., Hedley, M. J., Gregg, P. E. H., and Currie, L. D. (1997). Effect of phosphate fertiliser type on the accumulation and plant availability of cadmium in grassland. *Nutrient Cycling in Agroecosystems* **47**, 169-178.

Loganathan, P., Mackay, A. D., Lee, J., and Hedley, M. J. (1995). Cadmium distribution in hill pastures as influenced by 20 years of phosphate fertiliser application and sheep grazing. *Australian Journal of Soil Research* **33**, 859-871.

Lund, L. J., Betty, E. E., Page, A. L., and Elliott, R. T. (1981). Occurrence of naturally high cadmium levels in soils and its accumulation by vegetation. *Journal of Environmental Quality* **10**, 551-556.

Ma, L. Q., Rao, G. N. (1997). Chemical fractionation of cadmium, copper, nickel, and zinc in contaminated soils. *Journal of Environmental Quality* **26**, 259-264.

MacLean, A. J. (1976). Cadmium in different plant species and its availability in soils as influenced by organic matter and addition of lime, P, Cd and Zn. *Canadian Journal of Soil Science* **56**, 129-138.

Mahler, R. F., Bingham, F. T., Sposito, G., and Page, A. L. (1980). Cadmium-enriched sewage sludge application to acid and calcareous soils: Relation between treatment, cadmium in saturation extracts, and cadmium uptake. *Journal of Environmental Quality* **9**, 359-364.

Maier, N. A., McLaughlin, M. J., Heap, M., Butt, M., Smart, M. K., and Williams, C. M. J. (1997). Effect of current-season application of calcitic lime on soil pH, yield and cadmium concentration in potato (*Solanum tuberosum* L.) tubers. *Nutrient cycling in Agroecosystems* **47**, 29-40.

Mann, S. S., and Ritchie, G. S. P. (1993). The influence of pH on the forms of cadmium in four West Australian soils. *Australian Journal of Soil Research* **31**, 255-270.

Mann, S. S., and Ritchie, G. S. P. (1994). Changes in the forms of cadmium with time in some Western Australian soils. *Australian Journal of Soil Research* **32**, 241-250.

Marschner, H., Romheld, V., Horst, W. J., and Martin, P. (1986). Root induced changes in rhizosphere: Importance for the mineral nutrition of plants. *Z. Pflanzenernahr. Bodenk.*, **149**, 441-456.

McBride, M. B., Tyler, L. D., and Hovde, D. A. (1981). Cadmium adsorption by soils and uptake by plants as affected by soil chemical properties. *Soil Science Society of America Journal* **45**, 739-744.

McBride, M., Sauve, S., and Hendershot, W. (1997). Solubility control of Cu, Zn, Cd and Pb in contaminated soils. *European Journal of Soil Science* **48**, 337-346.

McGrath, S. P. (1986). The range of metal concentrations in topsoils of England and Wales in relation to soil protection guidelines. *Trace Substances in Environmental Health* **20**, 242-252.

McGrath, S. P., and Lane, P. W. (1989). An explanation for the apparent losses of metals in a long term field experiment with sewage sludge. *Environmental Pollution* **60**, 235-256.

McIntosh, P. D., Hewitt, A. E., Giddens, K., and Taylor, M. D. (1997). Benchmark sites for assessing the chemical impacts of pastoral farming on loessial soils in southern New Zealand. *Agriculture, Ecosystems and Environments* **65**, 267-280.

McKeaque, J. A., and Day, J. M. (1966). Dithionite and oxalate-extractable Fe and Al as aids in differentiating various classes of soils. *Canadian Journal of Soil Science* **46**, 13-22.

McLaren, R. G., and Crawford, D. V. (1973a). Studies on soil copper: I. The fractionation of copper in soil. *Journal of Soil Science* **24**, 173-181.

McLaren, R. G., and Crawford, D. V. (1973b). Studies on copper: II. The specific sorption of copper by soils *Journal of Soil Science* **24**, 443-452.

McLaren, R. G., Lawson, D. M., and Swift, R. S. (1986). Sorption and desorption of cobalt by soils and soil components. *Journal of Soil Science* **37**, 413-426.

McLaren, R. G., Swift, R. S., and Quin, B. F. (1984). EDTA-extractable copper, zinc, and manganese in soils of the Canterbury Plains. *New Zealand Journal of Agricultural Research* **27**, 207-217.

McLaren, R. G., Backes, C. A., Rate, A. W., and Swift, R. G. (1998). Cadmium and cobalt desorption kinetics from soil clays: Effect of sorption period. *Soil Science Society of America Journal* (In press).

McLaughlin, M. J., and Tiller, K. G. (1994). Chloro-complexation of cadmium in soil solutions of saline/sodic soils increases phyto-availability of cadmium. *Transactions 15th World Congress of Soil Science* **3b**, 195-196.

McLaughlin, M. J., Maier, N., Williams, C. M. J., Tiller, K.G., and Smart, M. K. (1993). Cadmium accumulation in potato tubers - occurrence and management. In 'Proceedings 7th National Potato Research Workshop, Ulverstone, May 1993.' (Ed. J. Fennell) pp. 208-213. (Tasmanian Department of Primary Industry: Launceston.)

McLaughlin, M. J., Palmer, L.T.,Tiller, K.G., Beech, T.A., and Smart, M.K. (1994a). Increased soil salinity causes elevated cadmium concentrations in field-grown potato tubers. *Journal of Environmental Quality* **23**, 1013-1018.

McLaughlin, M. J., Williams, C. M. J., McKay, A., Kirkman, R., Gunton, J., Jackson, K .J., Thompson, R., Dowling, B., Partington, D., Smart, M. K., and Tiller, K. G. (1994b). Effect of cultivar on uptake of cadmium by potato tubers. *Australian Journal Agricultural Research* **45**, 1483-1495.

McLaughlin, M. J., Maier, N. A., Freeman, K., Tiller, K. G., Williams, C. M. J., and Smart, M. K. (1995). Effect of potassic and phosphatic fertiliser type, phosphatic fertiliser Cd content and additions of zinc on cadmium uptake by commercial potato crops. *Fertiliser Research* **40**, 63-70.

McLaughlin, M. J., Tiller, K. G., Naidu, R., and Stevens, D. P. (1996). Review: the behaviour and environmental impact of contaminants in fertilisers. *Australian Journal of Soil Research* **34**, 1-54.

McLaughlin, M. J., Maier, N. A., Rayment, G. E., Sparrow, L. A., Berg, G., McKay, A., Milham, P., Merry, R. H., and Smart, M. K. (1997). Cadmium in Australian potato tubers and soils. *Journal of Environmental Quality* **26**, 1644-1649.

Mench, H., Baize, D., and Mocguot, B. (1997). Cadmium availability to wheat in five soil series from the Yonne district, Burgundy, France. *Environmental Pollution* **95**, 93-103.

Mench, M., and Martin, E. (1991). Mobilization of cadmium and other metals from two soils by root exudates of *Zea mays* L., *Nicotiana tabacum* L. and *Nicotiana rustica* L. *Plant and Soil* **132**, 187-196.

Merry, R. H. (1988). Investigations on cadmium in South Australia: Rainfall, soils, cereals, pastures and soil-plant interactions. Natl. Symp. On 'Cadmium Accumulations in Australian Agriculture. Canberra, 1-2 March 1988. (Eds J. Simpson and B. Curnow.) pp. 62-79. (Australian Govt. Publ. Service: Canberra.)

Merry, R. H., and Tiller, K. G. (1991). Distribution of cadmium and lead in an agricultural region near Adelaide, South Australia. *Water, Air and Soil Pollution* **57-58**, 171-180.

Miller, J. E., Hassett, J. J., and Koeppe, D. E. (1976). Uptake of cadmium by soybeans as influenced by soil cation exchange capacity, pH, and available phosphorus. *Journal of Environmental Quality* **5**, 157-160.

Mitchell, L. G., Grant, C. A., and Racz, G. J. (1997). Phytoavailability of cadmium in soils treated with nitrogen fertilisers. *In* Proceedings of Fourth International Conference on the Biogeochemistry of Trace Metals pp. 131-132. San Francisco, 23 - 27 June 1997.

Moraghan, J. T. (1993). Accumulation of cadmium and selected elements in flax seed grown on a calcareous soil. *Plant and Soil* **150**, 61-68.

Morgan, H., and Alloway, B. J. (1984). The value of soil chemical extractants for predicting the availability of cadmium to vegetables. *In* 'Trace Substances and Environmental Health XVIII'. (Ed D.D. Hemphill.) pp 539-547. (University of Missouri, Columbia.)

Mortvedt, J. J., Mays, D. A., and Osborn, G. (1981). Uptake by wheat of cadmium and other heavy metal contaminants in phosphate fertilizers. *Journal of Environmental Quality* **10**, 193-197.

Mulla, D. J., Page, A. L., and Ganje, T. J. (1980). Cadmium accumulations and bioavailability in soils from long-term phosphorus fertilization. *Journal of Environmental Quality* **9**, 408-412.

Mullins, G. L., and Sommers, L. E. (1986). Characterisation of cadmium and zinc in four soils treated with sewage sludge. *Journal of Environmental Quality* **15**, 382-387.

Murphy , J., and Riley, J. P. (1962). A modified single solution method for the determination of phosphate in natural waters. *Analytica Chimica Acta* **27**, 31-36.

Naidu, R., Bolan, N. S., Kookana, R. S., and Tiller, K. G. (1994). Ionic-strength and pH effects on the sorption of cadmium and the surface charge of soils. *European Journal of Soil Science* **45**, 419-429.

Narwal, R. P., and Singh, B. R. (1995). Sorption of cadmium, zinc, copper and lead by soils developed on alum shales and other material. *Norwegian Journal of Agricultural Sciences* **9**, 177-188.

Navrot, J., Singer, A., and Banin, A. (1978). Adsorption of cadmium and its exchange characteristics in some Israeli soils. *Journal of Soil Science* **29**, 505-511.

Neil, R. H., and Sposito, G. (1986). Effects of soluble organic matter and sewage sludge amendments on cadmium sorption by soils at low cadmium concentrations. *Soil Science* **142**, 164-172.

New Zealand Soil Bureau. (1968). Soils of New Zealand - Part 3. New Zealand Soil Bureau Bulletin 26(3).

Nicholson, F. A., Jones, K. C., Johnston, A. E. (1995). Evidence for the leaching of surface deposited cadmium in agricultural soils. *In* OECD Proceedings on 'Fertilizers as a source of cadmium' pp.218-231. (Sweden 16-20 October 1995.)

Novozamsky, I., Lexmond, T. H. M., and Houba, V. J. G. (1993). A single extraction procedure for evaluation of uptake of some heavy metals by plants. *International Journal of Environmental Analytical Chemistry* **51**, 47-58.

Nriagu, J. O. (1980). Production, uses and properties of cadmium. *In* 'Cadmium in the environment: part 1. Ecological cycling'. (Ed J. O Nriagu) (John Wiley and Sons, New York.)

O'Connor, G. A., O'Connor, C., and Cline, G. R. (1984). Sorption of cadmium by calcareous soils: influence of solution composition. *Soil Science Society of America Journal* **48**, 1244-1247.

Oborn, I., Jansson, G., and Johnsson, L. (1995). A field study on the influence of soil pH on trace element levels in spring wheat (*Triticum aestivum*), potatoes (*Solanum tuberosum*) and carrots (*Daucus carota*). *Water, Air and Soil Pollution* **85**, 835-840.

OECD (1994). Organisation for economic cooperation and development risk reduction monograph No. 5. Cadmium. (Environmental directorate, Organisation for economic cooperation and development, Paris.)

Oliver, D. P., Schulz, J. E., Tiller, K.G., and Merry, R. H. (1993). The effect of crop rotations and tillage practices on cadmium concentrations in wheat grain. *Australian Journal of Agricultural Research* **44**, 1221-1234.

Oliver, D. P., Hannam, R., Tiller, K. G., Wilhelm, N. S., Merry, R. H., and Cozens, G. D. (1994). The effects of zinc fertilization on cadmium concentrations in wheat grain. *Journal of Environmental Quality* **23**, 705-711.

Oliver, D. P., Gartrell, J. W., Tiller, K.G., Correll, G. D., Cozens, G. D., and Youngberg, B. L. (1995). Differential responses of Australian wheat cultivars to cadmium concentrations in wheat grain. *Australian Journal Agricultural Research* **46**, 873-886.

Oliver, D. P., Wilhelm, N. S., McFarlane, J. D., the late Tiller, K.G., and Cozens, G. D (1997). Effect of soil foliar applications of zinc on cadmium concentration in wheat grain. *Australian Journal of Experimental Agriculture* **37**, 677-681.

Pacyna, J. M. (1987). 'Lead, Mercury, Cadmium and Arsenic in the Environment SCOPE 31'. (Eds Hutchinson, T. C., and Meema, K. M.) pp. 69-87 (John Wiley, Chichester.)

Padmanabham, M. (1983). Adsorption-desorption behaviour of copper(II) at the goethite-solution interface. *Australian Journal of Soil Research* **21**, 309-320.

Page, A. L., Chang, A. C., and El-Amamy, M. (1987). Cadmium levels in soils and crops of the United States. *In* 'Lead, mercury, cadmium and arsenic in the environment'. (Eds Hutchinson, T. C., and Meema, K. M) pp. 119-146. (John Wiley and Sons Press.)

Pardo, M. T. (1997). Influence of electrolyte on cadmium interaction with selected andisols and alfisols. *Soil Science* **162**, 733-740.

Pardo, M. T., and Guadalix, M. E. (1995). Cadmium sorption by two acid soils as affected by clearing and cultivation. *Communications in Soil Science and Plant Analysis* **26**, 289-302.

Pardo, M. T., and Guadalix, M. E. (1996). Zinc sorption-desorption by two Andepts: Effect of pH and support medium. *European Journal of Soil Science* **47**, 257-263.

Penner, G. A., Clarke, J., Bezte, L. J., and Leisle, D. (1995). Identification of RAPD markers linked to a gene governing cadmium uptake in durum wheat. *Genome* **38**, 543-547.

Petruzzelli, G., Guidi, G., and Lubrano, L. (1985). Ionic strength effect on heavy metal adsorption by soil. *Communications in Soil Science and Plant Analysis* **16**, 971-986.

Puls, R. W., and Bohn, H. L. (1988). Sorption of cadmium, nickel, and zinc by kaolinite and montmorillonite suspensions. *Soil Science Society of America Journal* **52**, 1289-1292.

Puls, R. W., Powell, R. M., Clark, D., and Eldred, C. J. (1991). Effects of pH, solid/solution ratio, ionic strength, and organic acids on Pb and Cd sorption on kaolinite. *Water, Air, and Soil Pollution* **58**, 423-430.

Quevauviller, P., Rauret, G., Muntau, H., Ure, A. M., Rubio, R., Lopez-Sanchez, J. F., Fiedler, H. D., and Griepink, B. (1994). Evaluation of a sequential extraction procedure for the determination of extractable trace metal contents in sediments. *Fresenius Journal of Analytical Chemistry* **349**, 808-814.

Ramos, L., Hernandez, L. M., and Gonzalez, M. J. (1994). Sequential fractionation of copper, lead, cadmium and zinc in soils from or near Donana National Park. *Journal of Environmental Quality* **23**, 50-57.

Rattan, R. K., and Sehgal, D. (1989). Investigations on cadmium adsorption on soil differing in physical and chemical characteristics. *Journal of Indian Society of Soil Science* **37**, 284-289.

Reddy, C. N., and Patrick, W. H. (1977). Effect of redox potential and pH on the uptake of cadmium and lead by rice plants. *Journal of Environmental Quality* **6**, 259-262.

Reid, J. D., and McDuffie, B. (1981). Sorption of trace cadmium on clay minerals and river sediments: effects of pH and Cd(II) concentrations in a synthetic river water medium. *Water, Air and Soil Pollution* **15**, 375-386.

Riffaldi, R., and Levi-Minzi, R. (1975). Adsorption and desorption of Cd on Humic Acid Fraction of Soils. *Water, Air, and Soil Pollution* **5**, 179-184.

Roberts, A. H. C., Longhurst, R. D., and Brown, M. W. (1994). Cadmium status of soils, plants, and grazing animals in New Zealand. *New Zealand Journal of Agricultural Research* **37**, 119-129.

Roberts, A. H. C., Longhurst, R. D., and Brown, M. W. (1995). Cadmium survey of South Auckland market gardens and Mid Canterbury wheat farms. Report to the New Zealand Fertiliser Manufacturers Research Association.

Rothbaum, H. P., Goguel, R. L., Johnston, A. E., and Mattingly, G. E. G. (1986). Cadmium accumulation in soils from long-continued applications of superphosphate. *Journal of Soil Science* **37**, 99-107.

Sakurai, K., and Huang, P. M. (1996). Influence of potassium chloride on desorption of cadmium sorbed on hydroxyaluminosilicate-montmorillonite complex. *Soil Science and Plant Nutrition* **42**, 475-481.

Santillan-Medrano, J., and Jurinak, J. J. (1975). The chemistry of lead and cadmium in soil: solid phase formation. *Soil Science Society of America Journal* **39**, 851-856.

Sauerbeck, D. R., and Styperek, B. (1985). Evaluation of chemical methods for assessing the Cd and Zn availability from different soils and sources. *In* 'Chemical Methods for Assessing Bio-available Metals in Sludges and Soils'. (Eds Leschber, R., Davis, R.D., and Hermite, P. L.) pp 49 - 67. (Elsevier Applied Science Publishers: London.)

Schnitzer, M., and Khan, S. U. (1978). 'Soil organic matter'. (Elsevier, Amsterdam.)

Schroeder, H. A. (1974). 'The poisons around us: toxic metals in food, air, and water'. By Fitzhenry and Whiteside Ltd., Ontario (Indiana University Press. Pub.).

Selim, H. M. (1992). Modelling the transport and retention of inorganics in soils. *Advances in Agronomy* **47**, 331-384.

Semu, E., and Singh, B. R. (1996). Accumulation of heavy metals in soils and plants after long-term use of fertilizers and fungicides in Tanzania. *Fertiliser Research* **44**, 241-248.

Shuman L. M. (1982). Separating soil iron and manganese oxide fractions for microelement analysis. *Soil Science Society of America Journal* **46,** 1099-1102.

Shuman, L. M. (1985). Fractionation method for soil microelements. *Soil Science* **140**, 11-22.

Sidle, R. C., and Kardos, L. T. (1977). Adsorption of copper, zinc, and cadmium by a forest soil. *Journal of Environmental Quality* **6**, 313-317.

Sillanpaa, M., and Jansson, H. (1992). Status of cadmium, lead, cobalt and selenium in soils and plants of thirty countries. *FAO Soils Bulletin* **65**.

Singh, S. S. (1979). Sorption and release of cadmium in some Canadian Soils. *Canadian Journal of Soil Science* **59**, 119-130.

Singh, B. R. (1990). Cadmium and fluoride uptake by oats and rape from phosphate fertiliser in two different soils. *Norwegian Journal of Agricultural Sciences* **4**, 239-249.

Singh, B. R. (1991). Unwanted components of commercial fertilizers and their agricultural effects. Proceedings of Fertiliser Society London, Dec, 2-28.

Singh, B. R., and Myhr, K. (1997). Cadmium leaching from cadmium-enriched fertiliser in field lysimeters. *In* Proceedings of Fourth International Conference on the Biogeochemistry of Trace Metals pp. 105-106. San Francisco, 23 - 27 June 1997.

Singh, B. R., and Steinnes, E. (1976). Uptake of trace elements by barley in Zn-polluted soils. II. Lead, cadmium, mercury, selenium, arsenic, chromium and vanadium in barley. *Soil Science* **121**, 38-43.

Singh, S. P., and Nayyar, V. K. (1990). Accumulation characteristics of cadmium and its upper critical levels in selected vegetables species. *International Journal of Environmental Studies* **36**, 199-204.

Singh, D., McLaren, R. G., and Cameron, K. C. (1997). Desorption of native and added zinc from a range of New Zealand soils in relation to soil properties. *Australian Journal of Soil Research* **35**, 53-66.

Sloan, J. J., Dowdy, R. H., Dolan, M. S., and Linden, D. R. (1997). Long-term effects of biosolids on heavy metal bioavailability in agricultural soils. *Journal of Environmental Quality* **26**, 966-974.

Smilde, K. W., Van Luite, B., and Van Driel, W. (1992). The extraction by soil and absorption by plants of applied zinc and cadmium. *Plant and Soil* **143**, 233-238.

Smith, S. R. (1994). Effect of soil pH on availability of metals in sewage sludge-treated soils. II. Cadmium uptake by crops and implications for human dietary intake. *Environmental Pollution* **86**, 5-13.

Smolders, E., and McLaughlin, M. J. (1996). Effect of Cl on Cd uptake by Swiss Chard in nutrient solutions. *Plant and Soil* **179**, 57-64.

Soltanpour, P. N., and Schwab, A. P. (1977). A new soil test for the simultaneous extraction of macro- and micro-nutrients in alkaline soils. *Communications in Soil Science and Plant Analysis* **8**, 195-207.

Soon, Y. K., and Bates, T. E. (1982). Chemical pools of cadmium, nickel and zinc in polluted soils and some preliminary indications of their availability to plants. *Journal of Soil Science* **33**, 477-488.

Soon, Y. K., and Abboud, S. (1993). Cadmium, chromium, lead, and nickel. *In* 'Soil sampling and methods of analysis'. (Ed M. R. Carter)., (Boca Raton: Lewis Publishers.)

Spark, K. M., Wells, J. D., and Johnson, B. B. (1995a). Characterizing trace metal adsorption on kaolinite. *European Journal of Soil Science* **46**, 633-640.

Spark, K. M., Wells, J. D., and Johnson, B. B. (1995b). Characterizing trace metal adsorption on oxides and oxyhydroxides. *European Journal of Soil Science* **46**, 621-631.

Sparrow, L. A., Salardini, A. A, and Bishop, A. C. (1993). Field studies of cadmium in potatoes (*Solanum tuberosum* L.). I. Effects of lime and phosphorus on cv. Russet Burbank. *Australian Journal of Agricultural Research* **44**, 845-853.

Sparrow, L. A., Salardini, A. A. and Johnstone, J. (1994). Field studies of cadmium in potatoes (Solanum tuberosum L.). III. Responses of c.v Russet Burbank to sources of banded potassium. *Australian Journal of Soil Research* **45**, 243-249.

Sparrow, L. A., Chapman, K. S. R., Parsley, D., Hardman, P. R., and Cullen, B. (1992) Response of potatoes (*Solanum tuberosum* cv. Russet Burbank) to band-placed and broadcast high cadmium phosphorus fertiliser on heavily cropped krasnozems in north-western Tasmania. *Australian Journal of Experimental Agriculture* **32**, 113-119.

Sposito, G. (1984). 'The Surface Chemistry of Soils.' (Oxford University Press, New York.)

Stahl, R. S., and James, B. R. (1991). Zinc sorption by B horizon soils as a function of pH. *Soil Science Society of America Journal* **55**, 1592-597.

Stevenson, F.J. (1982). 'Humus chemistry'. (Wiley-Interscience, New York, NY.)

Street, J. J., Lindsay, W. L., and Sabey, B. R. (1977). Solubility and plant uptake of Cd in soil amended with Cd and sewage sludge. *Journal of Environmental Quality* **6**, 72 - 77.

Street, J. J., Sabey, B. R., and Lindsay, W. L. (1978). Influence of pH, phosphorus, Cd, sewage sludge and incubation time on the solubility and plant uptake of Cd. *Journal of Environmental Quality* **7**, 286-290.

Swift, R.S., and McLaren, R.G. (1991). Micronutrient sorption by soils and soil colloids. *In* 'Interactions at the soil colloid-soil solution interface'. (Eds G.H. Bolt *et al.*) pp 257-292. (Kluwer Academic Publ. Dordrecht, the Netherlands.)

Syers, J. K., Mackay, A. D., Brown, M. W., and Currie, L. D. (1986). Chemical and physical characteristics of phosphate rock materials of varying reactivity. *Journal of the Science of Food and Agriculture* **37**, 1057-1064.

Symeonides, C., and McRae, S. G. (1977). The assessment of plant available cadmium in soils. *Journal of Environmental Quality* **6**, 120-123.

Taylor, M. D., and Theng, B. K. G. (1995). Sorption of cadmium by complexes of kaolinite with humic acid. *Communications in Soil Science and Plant Analysis* **26**, 765-776.

Tessier, A., Campbell, P. G. C., Bisson, M. (1979). Sequential extraction procedure for the speciation of particulate trace metals, *Analytical Chemistry* **51**, 844-850.

Thomas, G. M., and Harrison, H. C. (1989). Inheritance of cadmium concentrations in lettuce. *Journal of America Society of Horticulture Science* **114**,121-125.

Tichy, R., Nydl, V., Kuzel, S., and Kolar, L. (1997). Increased cadmium availability to crops on a sewage-sludge amended soil. *Water, Air and Soil Pollution* **94**, 361-372.

Tiller, K. G., Gerth, J., and Bruemmer, G. (1984a). The sorption of Cd, Zn and Ni by soil clay fractions. Procedures for partition of bound forms and their interpretation. *Geoderma* **34**, 1-16.

Tiller, K. G., Gerth, J., and Bruemmer, G. (1984b). The relative affinities of Cd, Ni and Zn for different clay fractions and goethite. *Geoderma* **34**, 17-35.

Tiller, K. G., Nayyar, V. K., and Clayton, P. M. (1979). Specific and non-specific sorption of Cd by soil clays as influenced by zinc and calcium. *Australian Journal Soil Research* **17**, 17-28.

Tills, A., and Alloway, B. J. (1983). The speciation of Cd and Pb in soil solutions from polluted soils. International conference on Heavy Metals in the Environment (Heidelberg).

Tjell, J. C., and Christensen, T. H. (1985). Evidence of increasing cadmium contents of agricultural soils. In: T. D. Lekkas (ed.) Heavy Metals in the Environment. Vol. II. CEP Consultants Ltd., Edinburgh, 391-393.

Tjell, J. C., and Hovmand, M. F. (1978). Metal concentrations in Danish arable soils. *Acta Agriculturae Scandinavia* **28**, 81-89.

Tjell, J. C., Hansen, J. A., Christensen, T. H., and Hovmand, M. J. (1981). Predictions of cadmium concentrations in Danish soils. The Second European Symposium on Characterisation, Treatment and Uses of Sewage Sludge. Vienna, 20-24 October 1980. (Eds P. L'Hermite and H. Ott) pp.650-664. (D. Reidel: London).

Ure, A. M., Quevauvillier, P., Muntau, H., and Griepink, B. (1993). Speciation of heavy metals in soils and sediments. An account of the improvement and harmonization of extraction techniques undertaken under the auspices of the BCR of the Commission of the European Communities. *International Journal of Environmental Analytical Chemistry* **51**, 135-151.

Venugopal, B., and Luckey, T. D. (1978). 'Metal toxicity in mammals 2'. Chemical toxicity of metals and metalloids. (Plenum Press, New York.)

Wakefield, Z. P. (1980). Distribution of cadmium in phosphate fertiliser processing. *Cadmium Seminar*. The Fertiliser Institute, Washington, 141-143.

Warren, J. H. (1996). *Nitrogen and heavy metal dynamics following the application of municipal sewage sludge to an acid forest* (*Pinus radiata*) soil. Thesis, Ph.D., Lincoln University, Lincoln, New Zealand.

Webb, M. (1975). Cadmium. *British Medical Bulletin* **31**, 246-250.

Whitten, M. G., and Ritchie, G. S. P. (1991). Calcium chloride extractable cadmium as an estimate of cadmium uptake by subterranean clover. *Australian Journal of Soil Research* **29**, 215-221.

WHO (1972). Evaluation of certain food additives and of the contaminants mercury, lead and cadmium (FAO Nutrition Meetings Report Series No 51 WHO Technical Report Series 505). Food and Agriculture Organisation of the United Nations, Rome, Italy.

Wilkens, B. J., and Loch, J. P. G. (1997). Accumulation of cadmium and zinc from diffuse immission on acid sandy soils, as a function of soil composition. *Water, Air and Soil Pollution* **96,** 1-16.

Willaert, G., and Verloo, M. (1992). Effects of various nitrogen fertilisers on the chemical and biological activity of major and trace elements in a cadmium contaminated soil. *Pedologie* **43**, 83-91.

Williams, C. H. (1974). Heavy metals and other elements in fertilizers - environmental considerations. *In* 'Fertilizers and the Environment'. (Ed. D. R. Leece.) pp. 123-30. (Australian Institute of Agricultural Science: Sydney).

Williams, C. H. (1977). Trace metals and superphosphate. Toxicity problems. *Journal of Australian Institute of Agricultural Science* **43**, 99-109.

Williams, C. H., and David, D. J. (1973). The effects of superphosphate on cadmium content of soils and plants. *Australian Journal of Soil Research* **11**, 43-56.

Williams, C. H., and David, D. J. (1976). The accumulation in soil of cadmium residues from phosphate fertilisers and their effect on the cadmium content of plants. *Soil Science* **121**, 86-93.

Xue, Q., and Harrison, H. C. (1991). Effect of soil zinc, pH, and cultivar on cadmium uptake in leaf lettuce (*Latuca sativa L. var. crispa*). *Communications in Soil Science and Plant Analysis* **22**, 975-991.

Yuan, G., and Lavkulich, L. M. (1997). Sorption behaviour of copper, zinc, and cadmium in response to simulated changes in soil properties. *Communications in Soil Science and Plant Analysis* **28**, 571-587.

Zachara, J. M., and Smith, S. C. (1994). Edge complexation reactions of cadmium on specimen and soil derived smectite. *Soil Science Society of America Journal* **58**, 762-769.

Zachara, J. M., Smith, S. C., Resch, C. T., and Cowan, C. E. (1992). Cadmium sorption to soil seperates containing layer silicates and iron and aluminium oxides. *Soil Science Society of America Journal* **56**, 1074-1084.

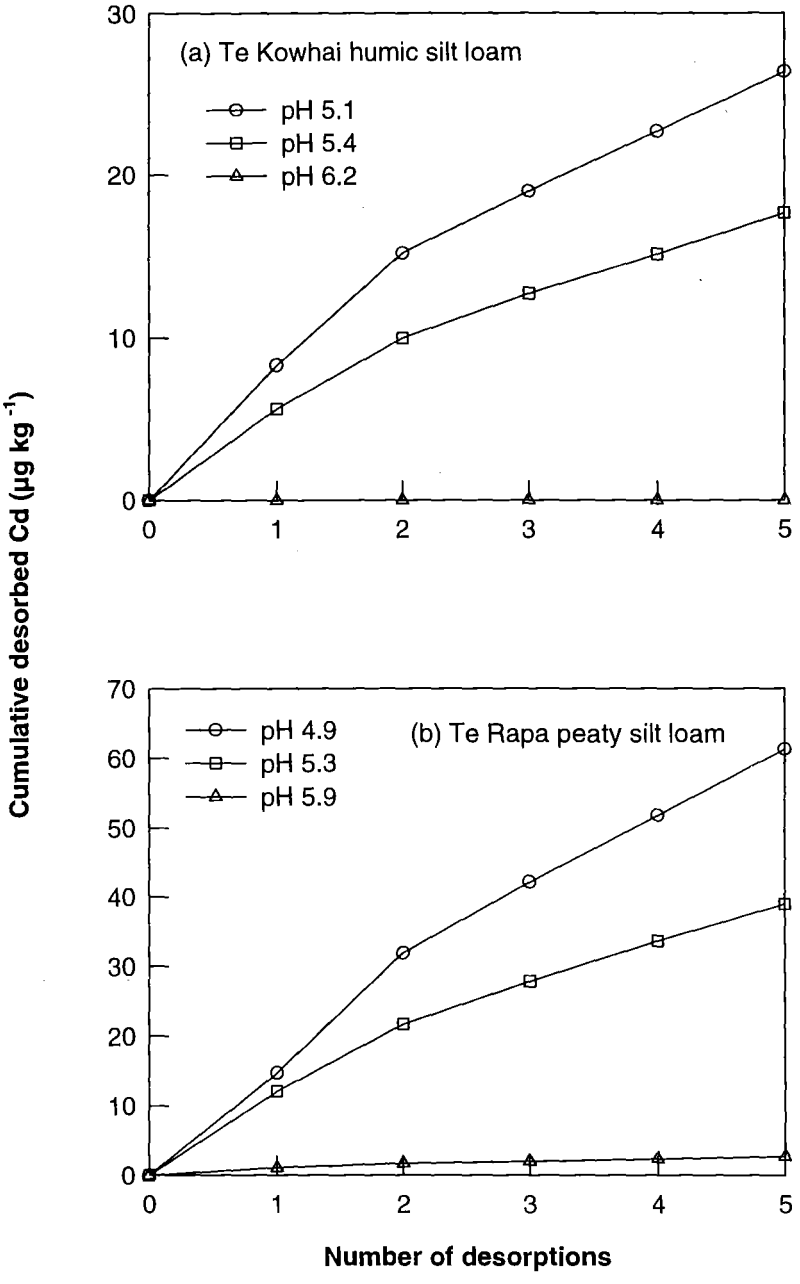
Zarcinas, B., and Nable, R. O. (1992). Boron and other impurities in South Australian fertilizers and soil amendments. CSIRO Aust. Division of Soils Divisional Rep. 118.

Zasoski, R. J. (1974). *Sorption and sorptive interactions of Cd and Zn on hydrous manganese oxide*. Thesis Ph.D., University of California, Davis.

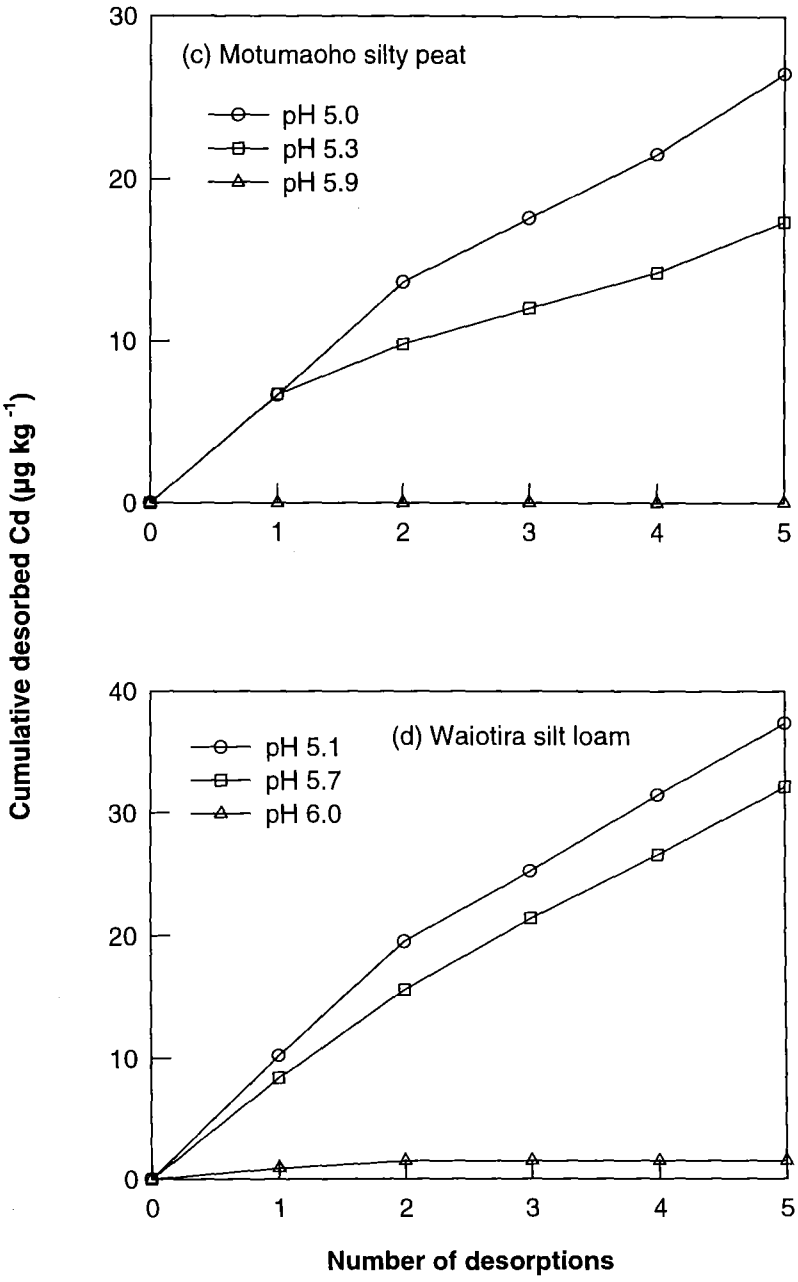
Zasoski, R. J., Burau, R. G. (1988). Sorption and sorptive interaction of cadmium and zinc on hydrous manganese oxide. *Soil Science Society of America Journal* **52**, 81-87.

Zhu, B., and Alva, A. K. (1993). Differential adsorption of trace metals by soils as influenced by exchangeable cations and ionic strength. *Soil Science* **155**, 61-66.

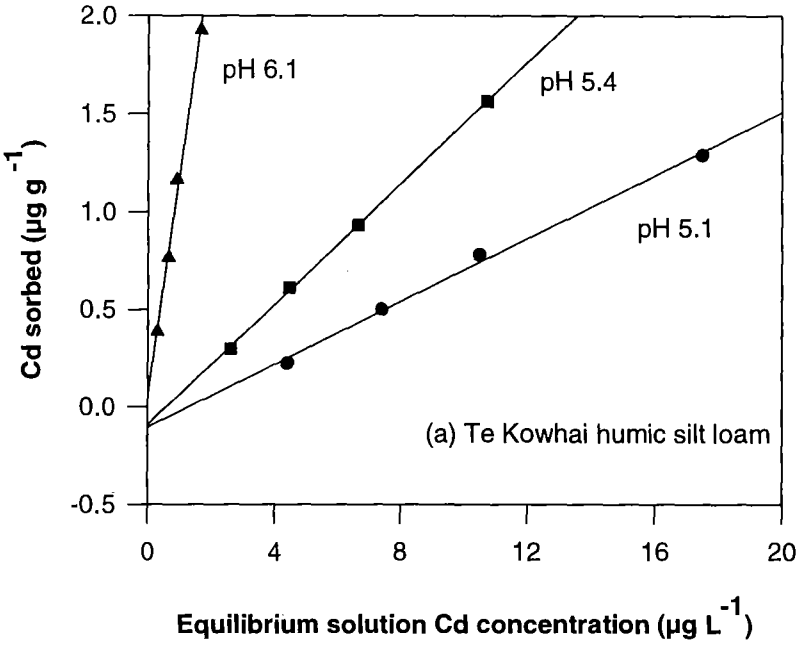
Ziper, C., Komarneni, S., and Baker, D. E. (1988). Specific cadmium sorption in relation to the crystal chemistry of clay minerals. *Soil Science Society of America Journal* **52**, 49-53.

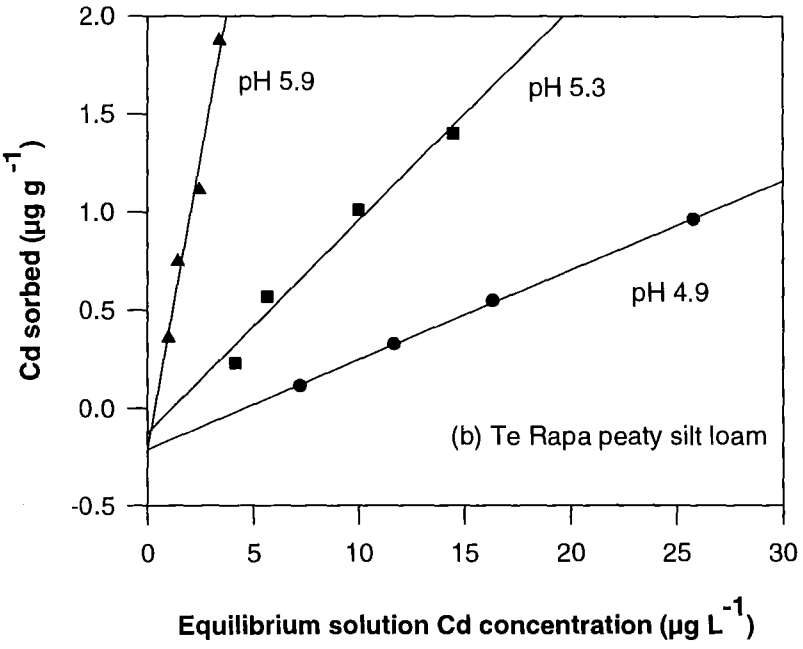


Appendix. 4.1 Effect of pH on cumulative desorption of native Cd from (a) Te Kowhai humic silt loam and (b) Te Rapa peaty silt loam.

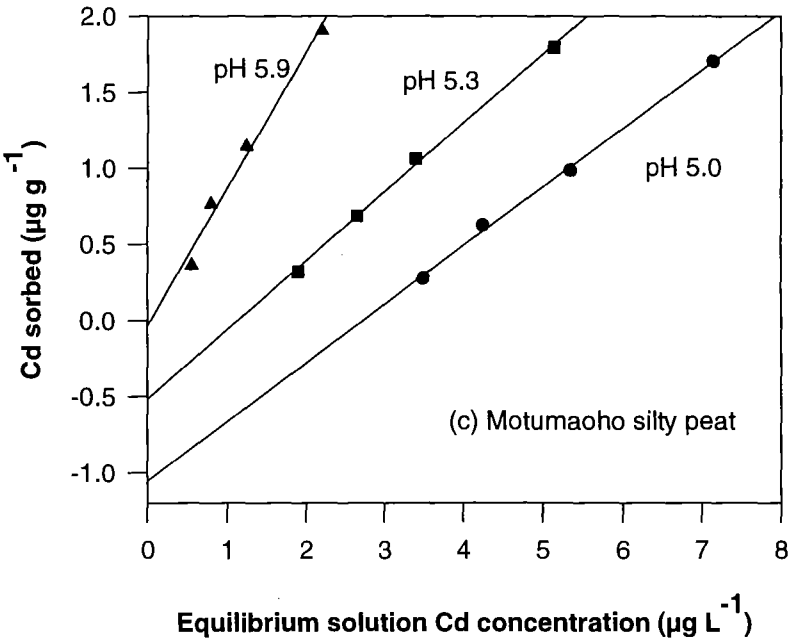


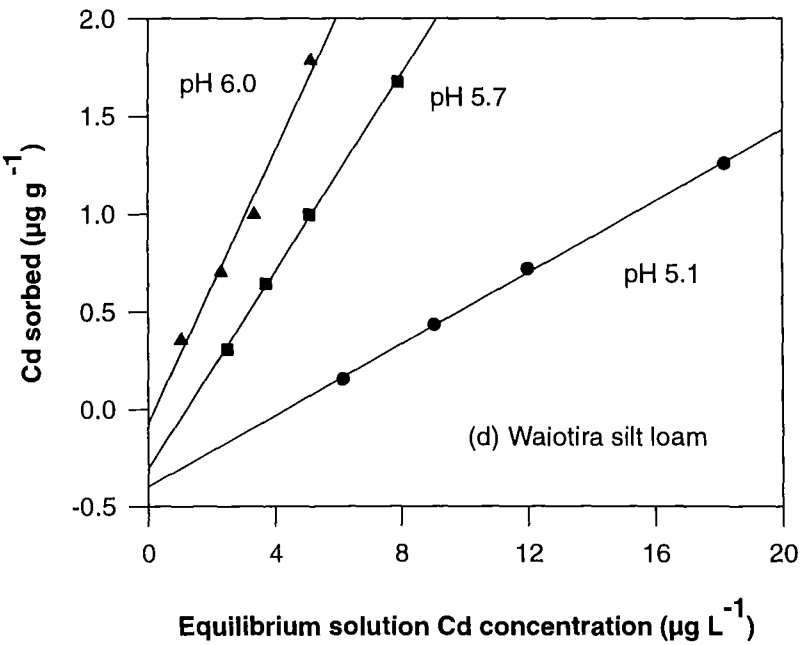
Appendix. 4.1 Effect of pH on cumulative desorption of native Cd from (c) Motumaoho silty peat and (d) Waiotira silt loam.



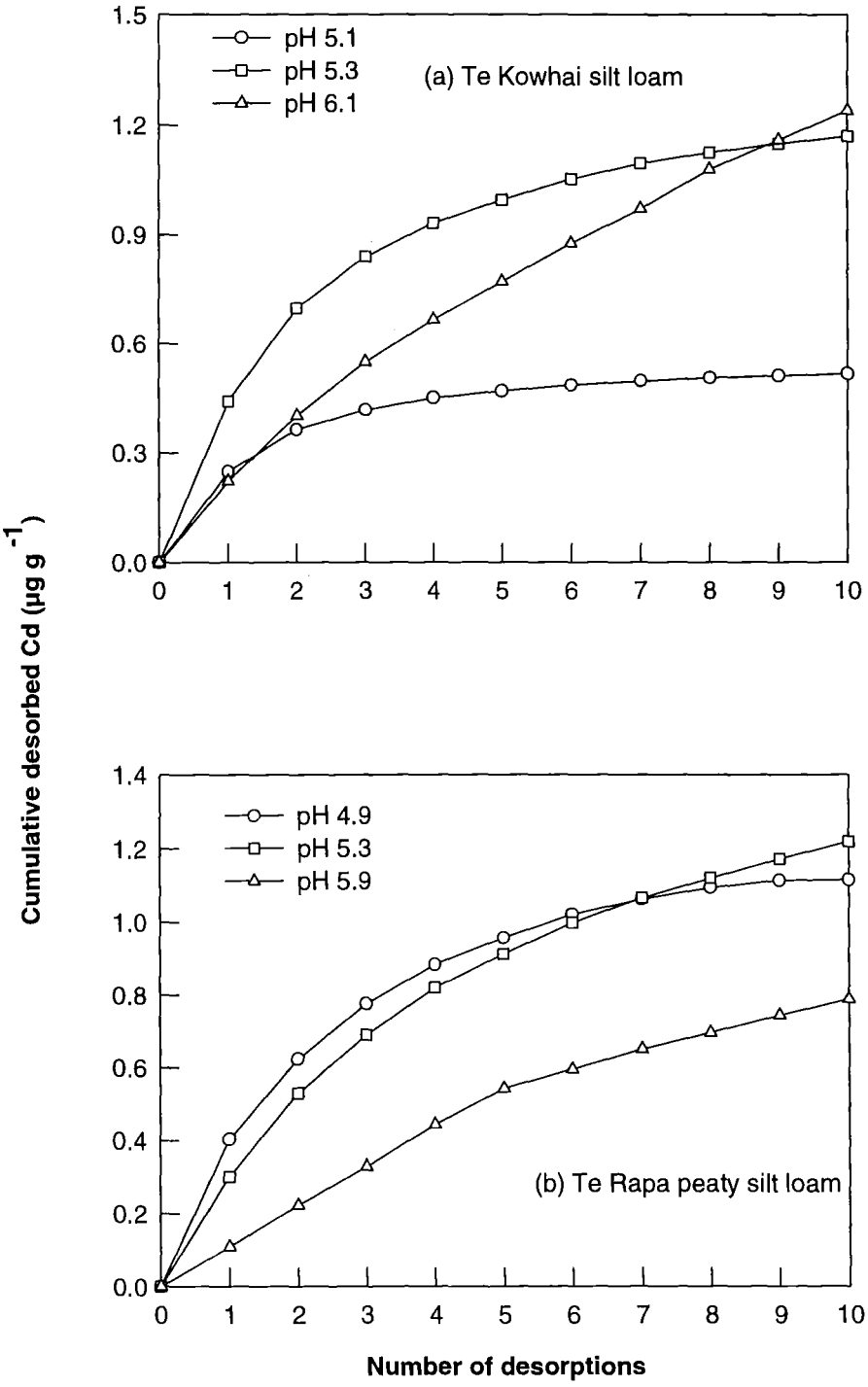


Appendix 4.2 Effect of pH on the sorption of Cd for (a) Te Kowhai humic silt loam (b) Te Rapa peaty silt loam.

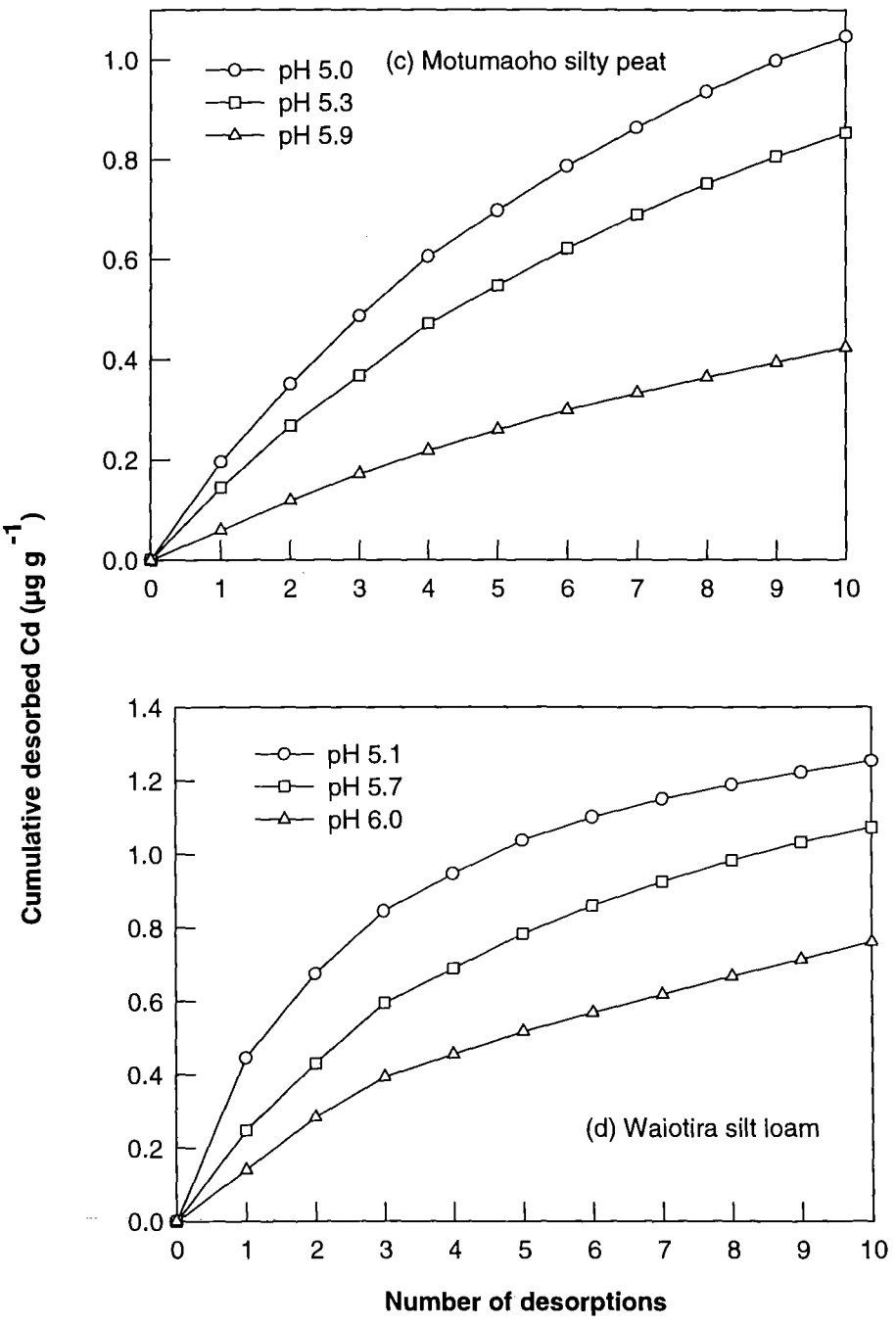




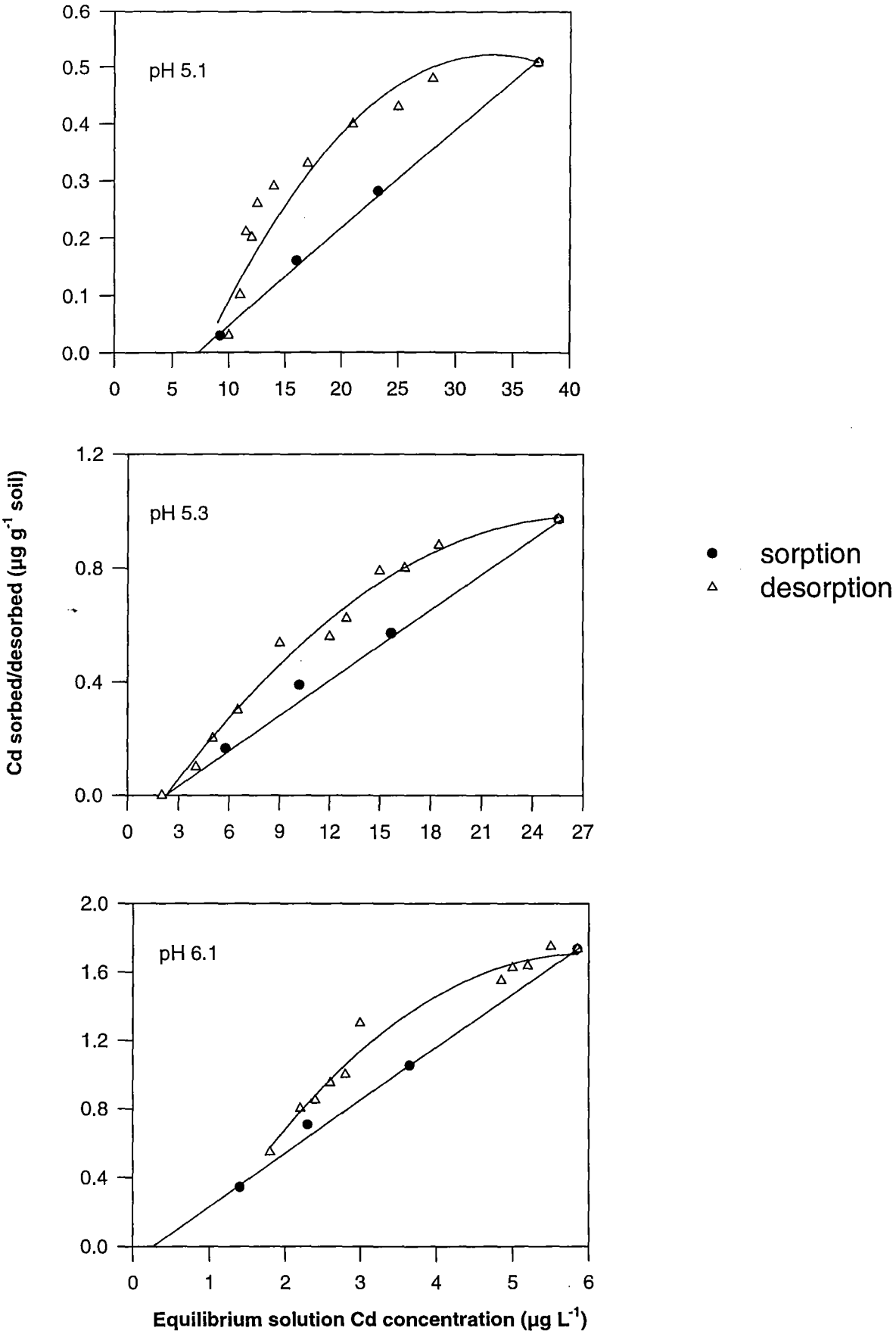
Appendix 4.2 Effect of pH on the sorption of Cd by (c) Motumaoho silty peat (d) Waiotira silt loam.



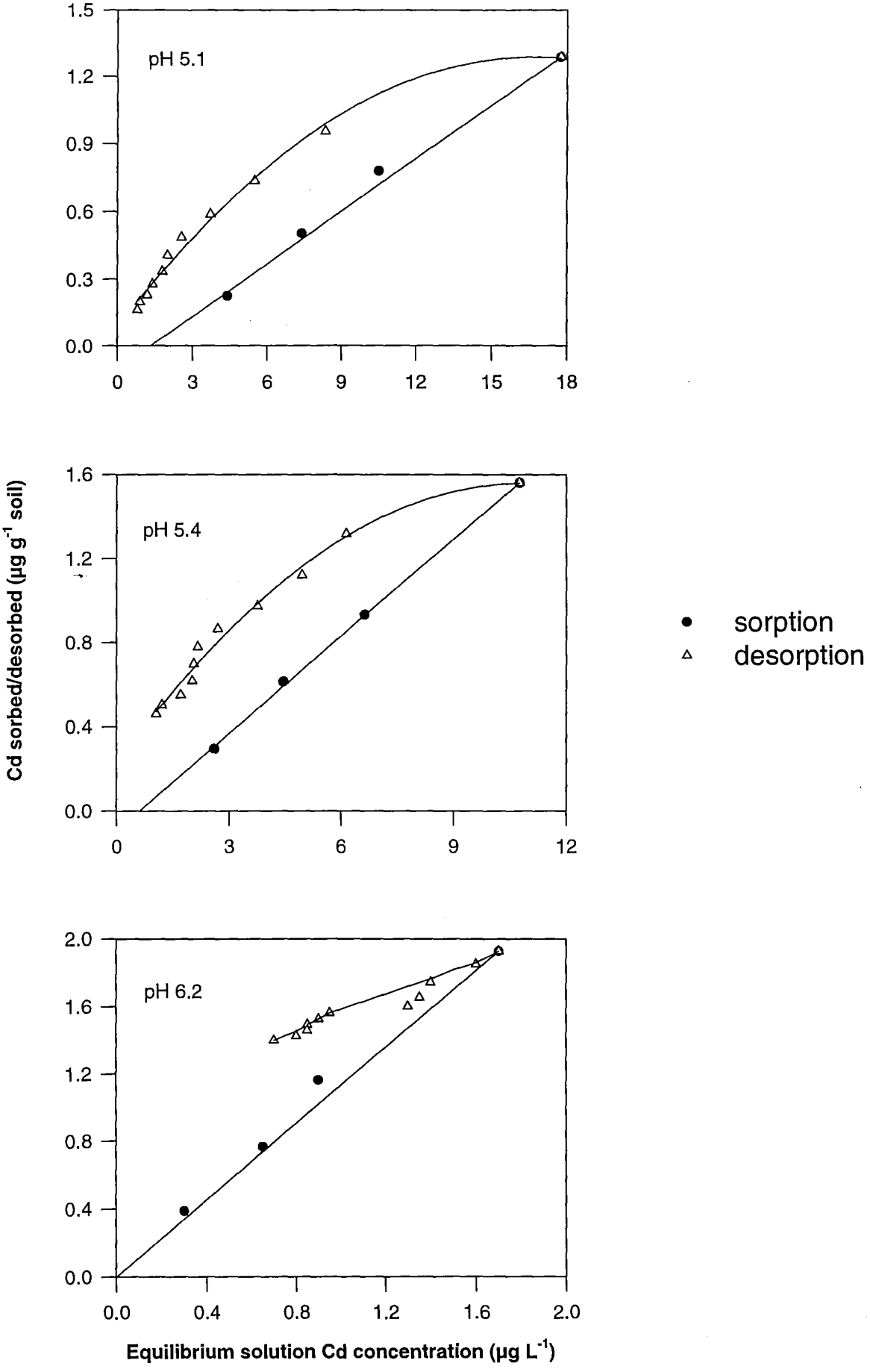
Appendix 4.3 Effect of pH on cumulative desorption of added Cd from (a) Te Kowhai silt loam and (b) Te Rapa peaty silt loam.



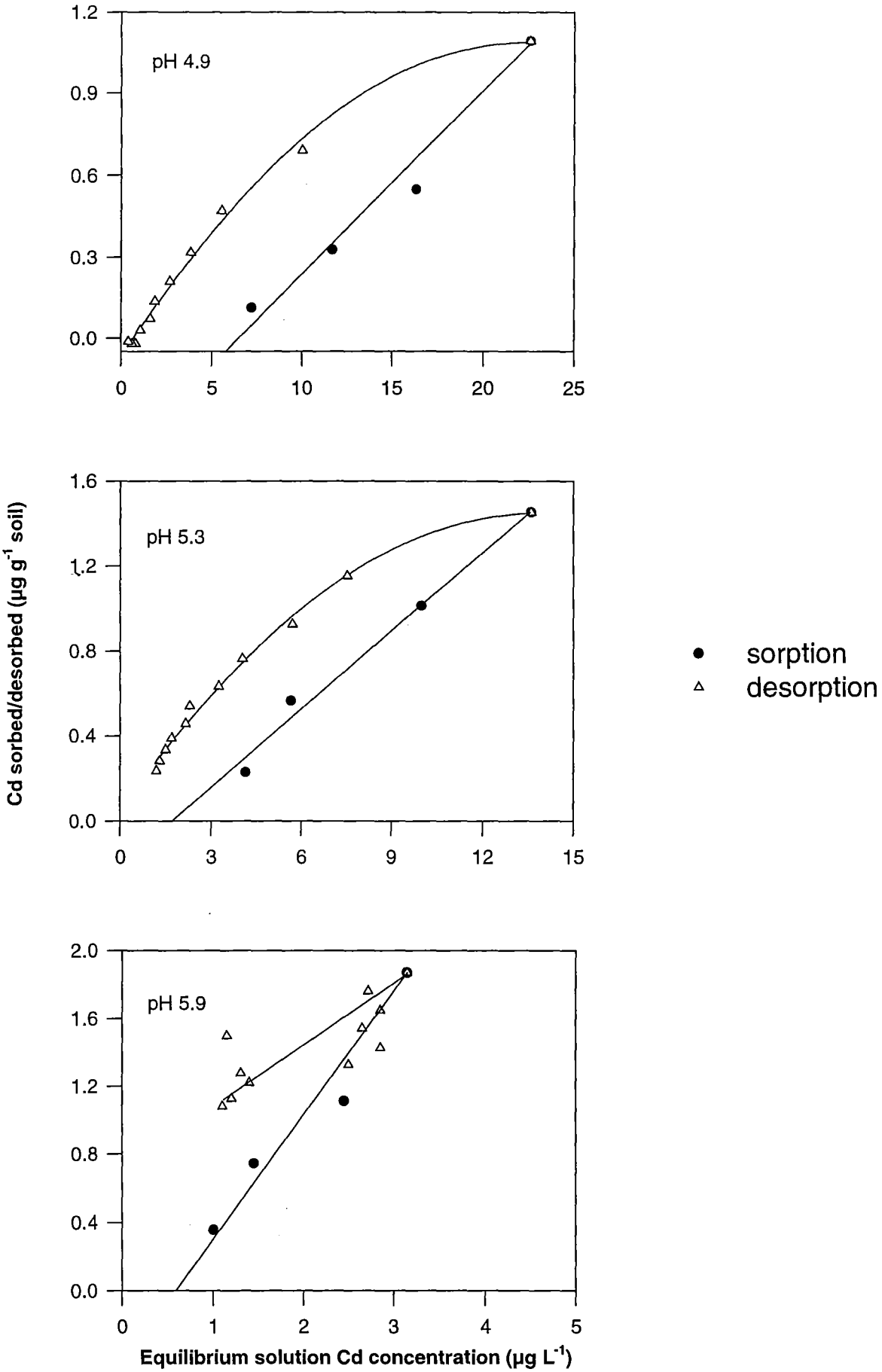
Appendix 4.3 Effect of pH on cumulative desorption of added Cd from (c) Motumaoho silty peat and (d) Waiotira silt loam.



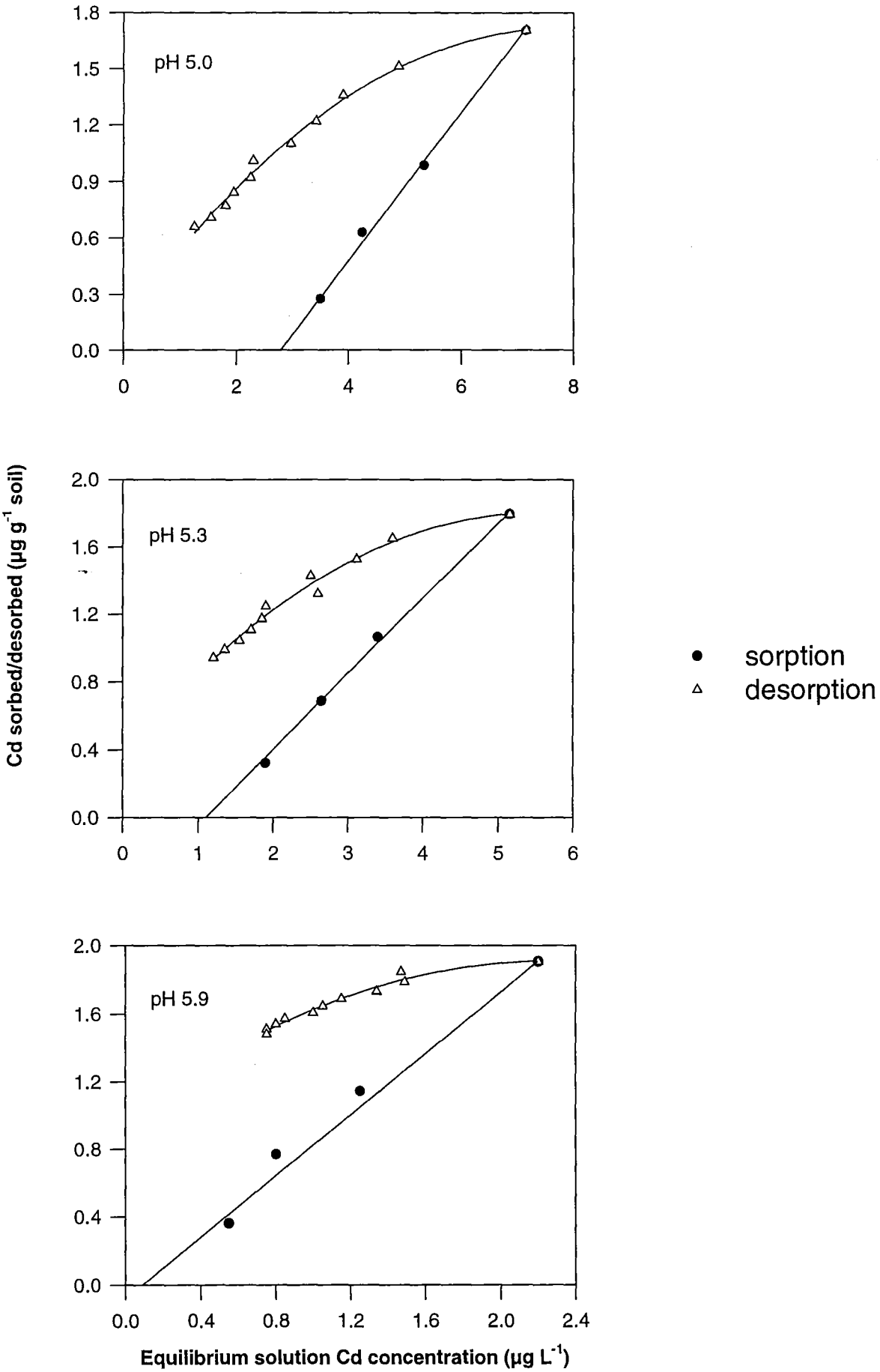
Appendix 4.4 Cadmium sorption (●) desorption (△) for the Te Kowhai silt loam.



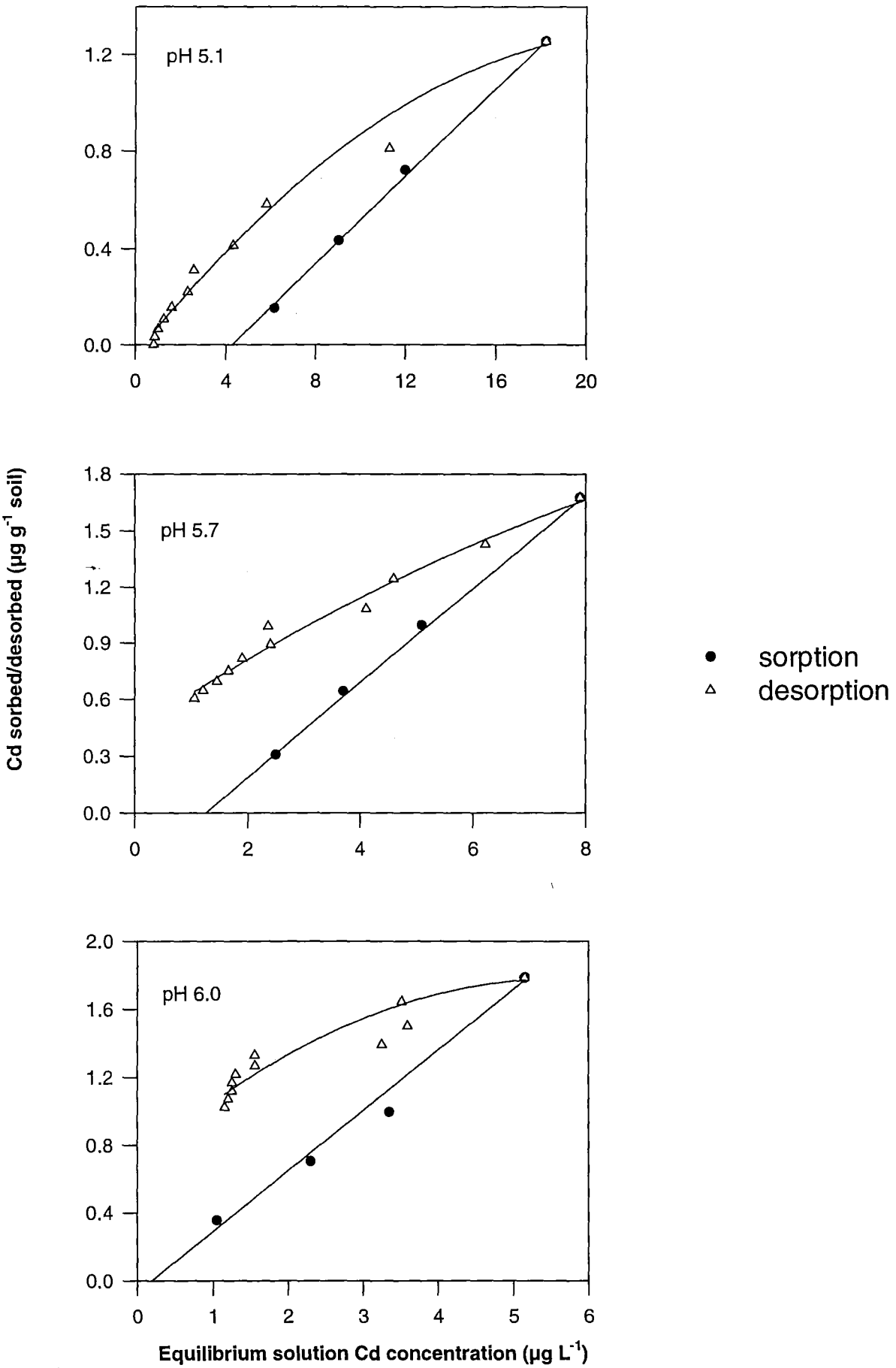
Appendix 4.4 Cadmium sorption (●) desorption (△) isotherms for the Te Kowhai humic silt loam.



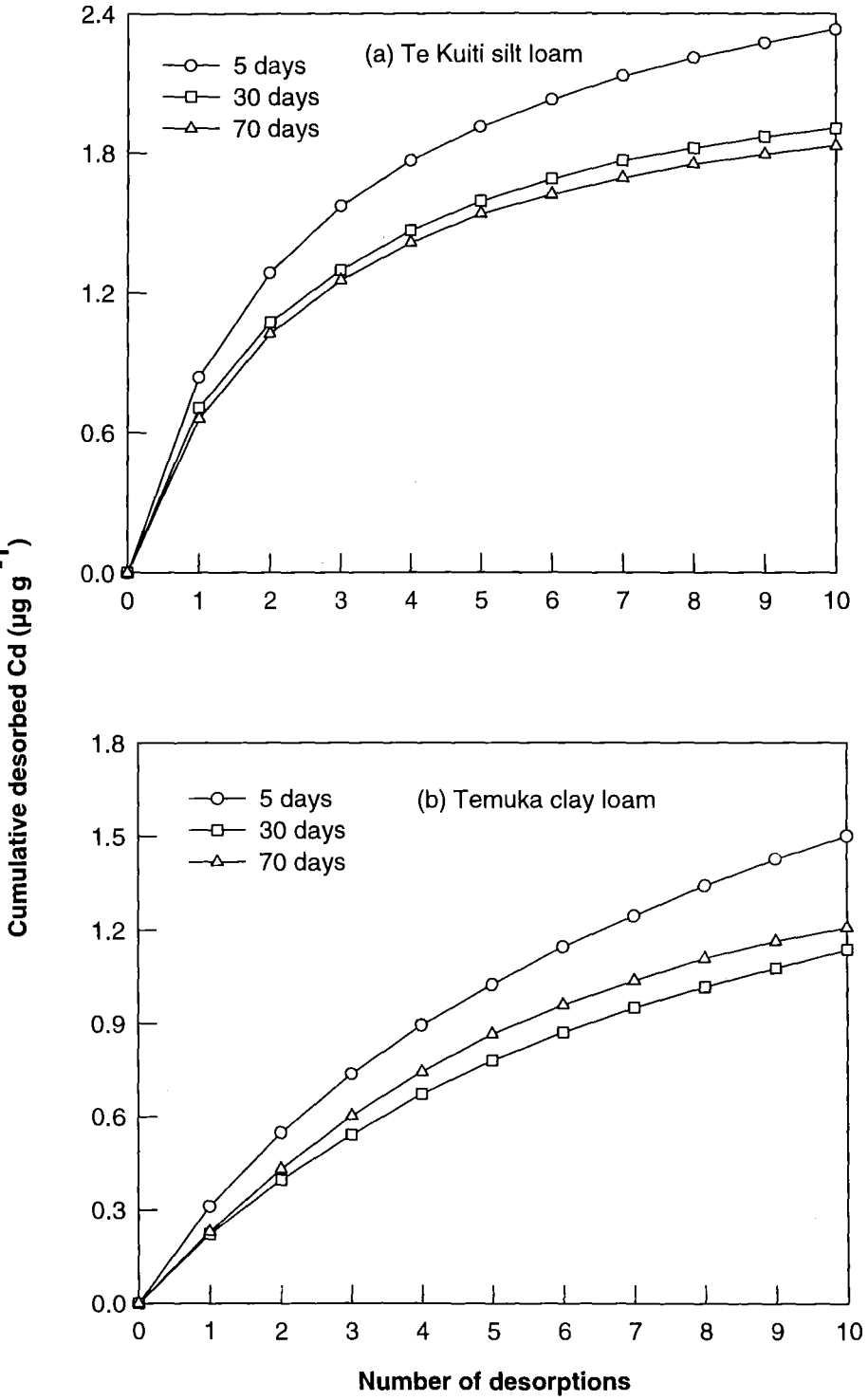
Appendix 4.4 Cadmium sorption (●) desorption (△) isotherms for the Te Rapa peaty silt loam.



Appendix 4.4 Cadmium sorption (●) desorption (△) isotherms for the Motumaoho silty peat.



Appendix 4.4 Cadmium sorption (●) desorption (△) isotherms for the Waiotira silt loam.



Appendix 4.5 Effect of contact time on cumulative desorption of added Cd from (a) Te Kuiti silt loam and (b) Temuka clay loam.

Appendix 6.1 Mean plant dry weights (g) and standard error of the mean for plant species

	Soil 1		Soil 2		Soil 3		Soil 4		Soil 5		Soil 6		Soil 7		Soil 8		Soil 9		Soil 10	
Species	mean	s.e.	mean	s.e.	mean	s.e.	mean	s.e.	mean	s.e.	mean	s.e.	mean	s.e.	mean	s.e.	mean	s.e.	mean	s.e.
Maize	**2.33**	0.21	**2.83**	0.04	**5.98**	0.75	**2.25**	0.22	**1.47**	0.10	**2.56**	0.40	**1.54**	0.12	**5.22**	1.16	**3.76**	0.51	**3.00**	0.13
Barley 1	**1.84**	0.11	**2.72**	0.19	**7.16**	0.57	**2.50**	0.09	**2.78**	0.35	**5.22**	0.30	**3.64**	0.35	**5.39**	0.22	**6.10**	0.25	**5.44**	0.21
Barley 2	**2.49**	0.30	**2.30**	0.44	**13.40**	1.16	**3.12**	0.40	**5.46**	0.73	**8.41**	1.18	**4.95**	0.23	**10.26**	0.48	**8.62**	0.48	**8.18**	0.87
Wheat 1	**1.67**	0.20	**1.85**	0.90	**8.02**	0.72	**3.40**	0.18	**2.06**	0.10	**3.79**	0.11	**2.41**	0.09	**6.27**	0.08	**4.33**	0.37	**5.13**	0.21
Wheat 2	**1.83**	0.33	**2.36**	0.42	**4.31**	0.51	**8.45**	1.96	**2.49**	0.72	**5.45**	0.36	**4.84**	0.41	**5.06**	0.72	**7.43**	0.92	**5.78**	0.81
Lettuce	**2.36**	0.17	**2.50**	0.31	**7.19**	0.52	**1.29**	0.25	**3.11**	0.04	**3.72**	0.27	**4.03**	0.38	**5.79**	0.91	**4.36**	0.53	**4.00**	0.22
Cabbage	**3.84**	0.34	**3.66**	1.13	**17.20**	1.12	**6.42**	1.18	**7.30**	1.13	**11.17**	0.85	**8.31**	0.57	**15.91**	1.93	**15.66**	0.17	**13.80**	0.39
Carrot top	**2.63**	0.26	**3.27**	0.35	**6.22**	0.15	**4.27**	0.04	**6.53**	0.07	**4.57**	0.52	**6.11**	0.59	**6.05**	0.05	**7.32**	0.58	**5.39**	0.94
Carrot root	**4.03**	0.73	**2.62**	0.17	**8.53**	0.58	**2.86**	0.53	**7.15**	0.45	**7.95**	0.40	**7.80**	0.23	**11.08**	0.65	**7.90**	0.22	**7.85**	0.75
Clover 1	**1.25**	0.17	**2.02**	0.19	**4.51**	0.96	**2.60**	0.32	**2.67**	0.26	**2.48**	0.52	**3.03**	0.35	**3.62**	0.25	**4.30**	0.29	**4.55**	0.24
Clover 2	**2.20**	0.06	**2.34**	0.23	**3.82**	0.80	**2.36**	0.21	**2.26**	0.38	**4.21**	0.87	**4.06**	0.22	**4.11**	0.31	**3.74**	0.12	**4.23**	0.84
Ryegrass 1	**1.24**	0.08	**1.83**	0.08	**4.18**	0.28	**1.83**	0.15	**1.12**	0.08	**2.81**	0.26	**1.72**	0.06	**2.69**	0.14	**2.71**	0.29	**2.31**	0.17
Ryegrass 2	**3.48**	0.23	**5.57**	1.16	**9.00**	0.67	**4.77**	0.23	**5.78**	0.47	**6.58**	0.39	**5.35**	0.18	**5.79**	0.67	**6.44**	0.53	**5.09**	0.19
Lucerne	**3.21**	0.39	**2.15**	0.22	**4.65**	0.43	**2.11**	0.33	**2.84**	0.33	**1.46**	0.16	**3.41**	0.79	**4.11**	0.10	**3.03**	0.19	**2.68**	0.31